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TRANSLITERATION

There is no ideal system of transli erating Russian; each has its advantag and disadvantages. For the translation Geokhimiya we have chosen the syste used by Chemical Abstracts, partly b cause of its wide acceptance by oth journals and partly because of certa advantages in alphabetization of names The principal differences between th system and others in common use are a follows:

Russian	Chem. Abs.	Othe
Х	kh	h
Ц	ts	tz
Щ	shch	sc
Ю	yu	iu
Я	ya	ia

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THE LAWS OF ISOMORPHISM

1. THE DISTRIBUTION OF Mg, Fe, Mn, Ca, Sr, Ba, Li, K, Rb AND SOME OTHER ELEMENTS N MINERALS CRYSTALLIZING FROM MAGMAS

V. I. LEBEDEV
Leningrad State University

(ABSTRACT)

In the paper it is proved that in the first high-temperature stages of crystallization only elements which are able to strengthen the lattice to increase its energy enter as isomorphous admixtures (a capture of elements is taking place). In the following relatively low-temperature crystallization states, usually as a result of a concentration increase, enter also elements which weaken the lattice and decrease its energy also enter as isomorphous admixtures (the elements are admitted). The prediction of one or the other behavior of the element, especially in the case of heterovalent isomorphism, is a more complicated task than the known rules of V. M. Goldschmidt permit.

---

1. As a factor complicating the composition of simple and complex compounds, isomorphism is a very important phenomenon in the behavior of many, and especially rare and dispersed elements. But in spite of the fact that the phenomenon of isomorphism has been studied for 140 years, in spite of the accumulation of vast empirical material and formulation of a series of rules, knowledge of the true laws of isomorphism still falls short of the requirements of modern science and technology. It is proposed in the present paper, by using factual material from a series of papers by different authors, to examine the reality of a generalization arising from the energy analysis of natural processes [8] and representing the development of a series of rules of isomorphism formulated earlier by Fersman [14] and Goldschmidt [5, 15]. A review of the already known material is the more necessary, as in some cases not all possible conclusions have been drawn from it, and in others the conclusions which have been reached are diametrically opposed.

2. The question of the distribution of Mg, Fe and some other elements

in silicates has been discussed by Ramberg and DeVore [16, 17]. These authors drew theoretical conclusions which will be only partially discussed here.

The observed regularities on which these papers are based are shown graphically in Fig. 1 [16, 17]. The compositions of the coexisting olivines and orthopyroxenes plotted on the diagram were obtained by refractive index measurements and the use of Kennedy's diagrams. It should be noted that the authors used a random collection of rock samples and as a result the most commonly occurring pairs of minerals plotted in the upper left-hand corner are represented by a small number of examples. The following additions have been made to the original Ramberg-DeVore diagram: 1) the olivine-pyroxene pairs have been numbered in the same sequence as in the authors' Table 1 [16], 2) the diagram has been divided into four fields and 3) specific names have been given to the olivines and pyroxenes.

According to the diagram, in pyroxenites, amphibolite sills, diabases and gabbros, forsterite, the magnesium-rich olivine, is associated with enstatite and bronzite. In these rocks the orthosilicate is, as a rule, enriched in Mg and the metasilicate, in Fe, or, less frequently, the Fe/Mg ratios in the two minerals are very similar. In syenites, and partly in iron-titanium ores, magnesium-poor fayalite is associated with hypersthene; i. e., the orthosilicate is enriched in Fe and the metasilicate in Mg, and the difference in the composition of the two minerals is considerable. In anorthosites, lamprophyres, norites and some other rocks, the difference between the composition of the orthosilicate enriched in Fe and the metasilicate enriched in Mg is slight or less pronounced.

In spite of the complex picture presented by the composition of the coexisting olivines and pyroxenes, Ramberg [17], after comparing the statistical distribution of the Fe/Mg ratios in olivines, pyroxenes, anthophyllites and talcs, i. e., in minerals with different silicate structures (independent tetrahedra, single and double chains and sheets), made a generalization to the effect that olivine is always the richest in iron and is followed (in decreasing Fe/Mg ratio) by pyroxene, anthophyllite and finally by the almost purely magnesian mineral, talc.

Ramberg ascribes this Fe-Mg partition to the exothermic effect of the base exchange reactions [17]:

$$\underset{\text{olivine}}{Mg_2SiO_4} + \underset{\text{pyroxene}}{2\,FeSiO_3} \longrightarrow \underset{\text{olivine}}{Fe_2SiO_4} + \underset{\text{pyroxene}}{2MgSiO_3} + \Delta H_1 \qquad (1)$$

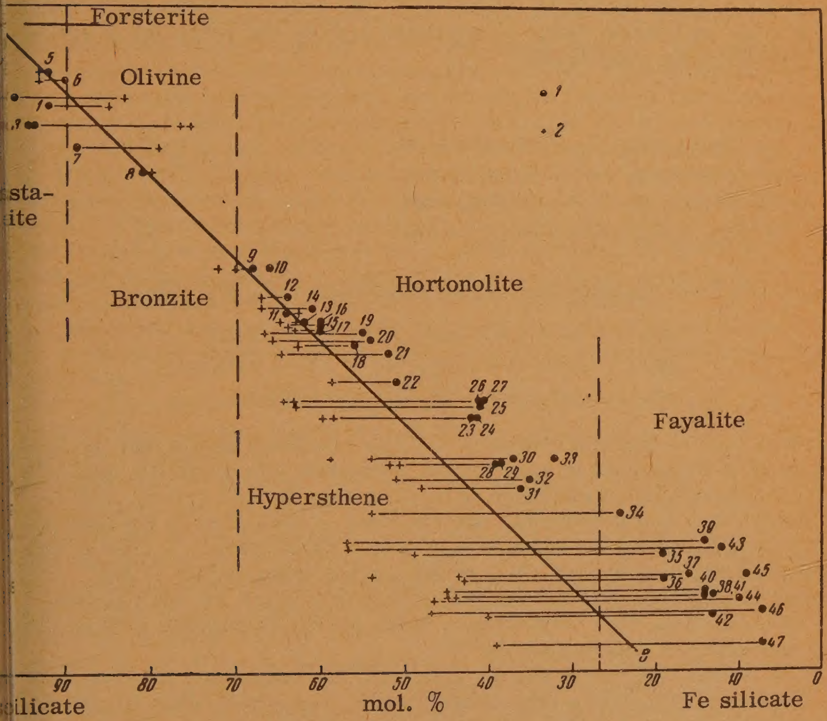
$$\underset{\text{pyroxene}}{7Mg\cdot SiO_3} + \underset{\text{anthophyllite}}{Fe_7Si_8O_{22}(OH)_2} \longrightarrow \underset{\text{pyroxene}}{7FeSiO_3} + \underset{\text{anthophyllite}}{Mg_7Si_8O_{22}} + \Delta H_2 \qquad (2)$$

$$\underset{\text{anthophyllite}}{3Mg_7Si_8O_{22}(OH)_2} + \underset{\text{minnesotaite}}{7Fe_3Si_4O_{10}(OH)_2} \longrightarrow \underset{\text{anthophyllite}}{3Fe_7Si_8O_{22}(OH)_2} + \Delta H_3 + \underset{\text{talc}}{7Mg_3Si_4O_{10}(OH)_2} + \Delta H_3 \qquad (3)$$

Indeed, in the first reaction, according to thermochemical investigations [19], $\Delta H_1 = -2.31 \pm 0.49$ kcal.

Comparing Ramberg's conclusion with the fact represented in the upper left-hand corner of the diagram (Fig. 1), which has been long known and considered as a confirmation of one of the rules of isomorphism formulated by Goldschmidt [5], it is impossible not to notice a contradiction, for, according to the above reactions governing the distribution of Fe and Mg, the enrichment of olivine in Fe and of pyroxene in Mg should be energetically

re advantageous, while according to the diagram (Fig. 1) the opposite
es place in the high temperature basic rocks. This contradiction be-
nes even sharper if it is noted that in the high temperature silicate syn-
sis a tendency is observed towards a higher Fe/Mg ratio in the melt than
he mineral in equilibrium with it [17].



1. Compositions of natural olivines coexisting with orthopyroxenes (after Ramberg and DeVore [16])

● -- orthosilicate + -- metasilicate

here appears to be only one way to resolve this contradiction. It is
ssary to assume that the distribution of Fe and Mg in the mineral se-
olivine-orthopyroxene-anthophyllite-talc, is determined in accord-
with the thermodynamic laws by the energetics of base exchange re-
ns (1) - (3), leading to the formation of "pure" compounds, while the
radictory composition of coexisting olivines and pyroxenes is governed
by the energetics of isomorphism, leading to the formation of mixed
ounds. The energy characteristics of isomorphism follow from the
ergetic theory [8] and, as will be seen later, agree with the laws of
nodynamics. It is evident that if reaction (1) is exothermic

(ΔH_1 = -2.31 kcal.), so must be the following reaction:

$$(Mg_{2-n}Fe_n)SiO_4 + (Fe_{2-n} + Mg_n)Si_2O_6 \longrightarrow (Fe_{2-n}Mg_n)SiO_4 + \\ + (Mg_{2-n}Fe_n)Si_2O_6 + \Delta H_1' \qquad (1')$$

but here $\Delta H_1'$ is somewhat more than merely proportional to the numerical Mg/Fe ratio of reaction (1), for according to Le Chatelier and van't Hoff, solid solutions are stable only if their formation is accompanied by an exothermic effect [8].

However, besides reactions (1) and (1'), the actual process of crystallization of complex natural melts is regulated also by the reactions of formation of the following compounds:

$$2MgO + SiO_2 \longrightarrow Mg_2SiO_4 + \Delta H_4 \qquad (4)$$

$$2FeO + SiO_2 \longrightarrow Fe_2SiO_4 + \Delta H_5 \qquad (5)$$

$$Mg_2SiO_4 + SiO_2 \longrightarrow 2MgSiO_3 + \Delta H_6 \qquad (6)$$

$$Fe_2SiO_4 + SiO_2 \longrightarrow 2FeSiO_3 + \Delta H_7 \qquad (7)$$

It is known from thermochemical investigations [19, 20], that:

$$\Delta H_4 = -15{,}12 \pm 0{,}21 \text{ kcal. } \Delta H_5 = -11{,}3 \text{ kcal.}$$

$$\Delta H_6 = -2{,}62 \pm 0{,}28 \text{ kcal. } (\Delta Z_6 = -2{,}5 \pm 0{,}32 \text{kcal});$$

$$\Delta H_7 = -0{,}31 \pm 0{,}11 \text{kcal. } (\Delta Z_7 = -0{,}46 \text{kcal}).$$

A comparison of thermochemistry of these reactions shows that the heat of formation of ferrosilite is very low as compared with enstatite, and this explains the occasional occurrence of fayalite even in acid rocks. Moreover, the formation of magnesium orthosilicate (reaction 4) is energetically more advantageous than the formation of iron orthosilicate. In view of the fact that the ionization energy ($\Sigma\,\underline{i}$) of Mg and the ionic radius of Mg^{2+} ($\underline{r_k}$) are somewhat smaller than the corresponding values for Fe, this means that in ionic bonding, Mg^{2+} contributes more energy to both the orthosilicate and the metasilicate lattice than Fe^{2+}*.

In other words, Mg increases the energy of the lattice per unit cell and makes it more stable, while iron diminishes it, especially when entering into a metasilicate, and makes the lattice less stable. This is important under high temperature conditions when the kinetic energy of the moving

---

* The heat of formation $\underline{Q}$ ($\underline{Q} = -\Delta\underline{H}$) and the lattice energy $\underline{U}$ in ionic compounds depend on the characteristics of the constituent cations (energies of sublimation $\underline{S}$, ionization energy $\Sigma\,\underline{i}$, charge $\underline{w}$ and radius $\underline{r_k}$) and anions (dissociation energy $\underline{D}$ and the electron affinity $\Sigma\epsilon$, charge $\underline{w}$ and radius $\underline{r_a}$) and are determined by the equation:

$$\underline{Q} = \underline{U} - \underline{S} - \underline{D} - \Sigma\,\underline{i} + \Sigma\epsilon, \quad \underline{U} = k\,\frac{\Sigma\,\underline{nw.w}}{\underline{r_k} + \underline{r_a}}$$

articles is great* and the lattices forming in the melt must have high nergy to bond their structural units.

Because of all these contradictory factors, and first of all those follow- ng from the reaction (1) - (1'), on the one hand, and reactions (4) - (7), n the other, a given Fe/Mg ratio in the silicate melt leads to definite but ifferent ratios of these elements in the coexisting ortho- and metasilicates. hen Mg predominates over Fe in the melt and crystallization occurs at igh temperature, apart from the general cause of isomorphism (a slightly reater energy advantage of a mixed compound over a "pure" one), there is lso the need for strengthening the lattice (for a weakened lattice will be estroyed by the thermal motion of its component parts). Therefore, the rst minerals to crystallize will be enriched in Mg. Olivine usually crys- llizes before the orthopyroxenes, for forsterite releases more energy per ram-atom (2.16 kcal.) than enstatite (1.74 kcal.), [7, 8] and will be more rongly enriched in Mg. When Fe predominates over Mg in the melt, as syenites and Fe-Ti ores, which crystallize at lower temperatures and ssibly with a different order of crystallization, only the general cause of rmation of mixed compounds is important, while the need for strengthen- g the lattice becomes much less so. For this reason, in spite of reaction), rather large quantities of iron or iron metasilicate enter into the mag- sium metasilicate lattice, until it becomes too unstable.

3. The extensive empirical material on dispersed elements discussed in tail in the work of Nockolds and Mitchell [10] is summarized in the dia- am of Fig. 2.

The authors declare that in discussing the dispersed elements and their lation to the principal elements with similar ionic radii, they will follow ldschmidt's two rules:

a) If two ions have equal electrostatic charges (of the same sign) and e ionic radii, so that they can occupy the same position in a given crystal ttice, the ion with the smaller radius will enter into the lattice more adily than the ion with the larger radius. b) If two ions are comparable size but have different electrostatic charges of the same sign, the ion th the higher charge will enter into the lattice more easily than the one th the lower charge [10].

Having reviewed the factual material presented in Fig. 2 in light of these les, the authors conclude that, "The distribution of dispersed elements ong individual minerals of a given rock depends mainly on the type of the neral lattice and on the relative age of the minerals. The variation in e content of rare elements in a given mineral group from the earlier and om later rocks agrees, with few exceptions, with Goldschmidt's rules")].

The factual material not only confirms Goldschmidt's rules, and also rsman's rules, which state that the entry of an ion with a higher charge smaller size strengthens the lattice by increasing its energy, but makes

---

According to the kinetic theory, the energy of thermal motion of a parti- is E = (3/2) KT, where K is the Boltzmann constant ($1.38 \cdot 10^{-16}$ s/deg.) and T is absolute temperature. From this it is easy to see that heat energy of an ion in molten basic magma beginnong to crystallize at = 1500°C is $3.1 \cdot 10^{-13}$ ergs, and of acid magma beginning to crystallize T = 1100°C, $2.28 \cdot 10^{-13}$ ergs (about 4.5 and 3.3 kcal. per gram ion, pectively).

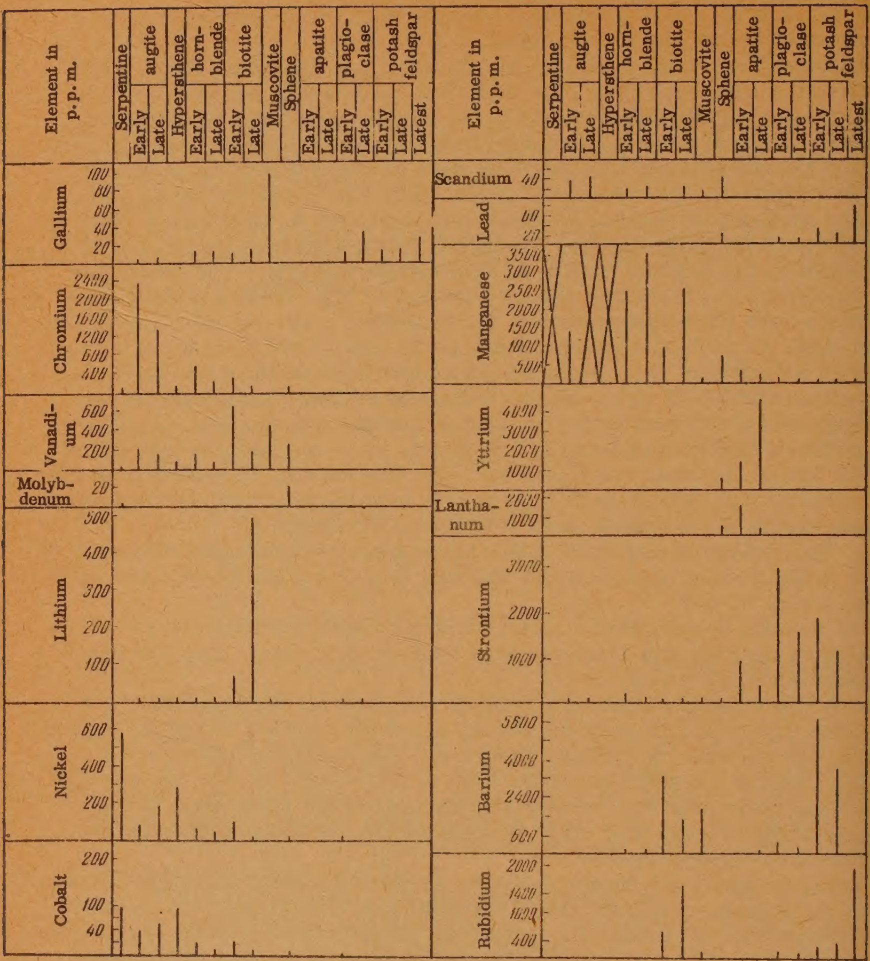


Fig. 2. Average content of rare elements in different minerals of Caledonian plutonites of Western Scotland (after Nockolds and Mitchell [10])

it possible also to extend these rules in light of the generalization discussed in the present paper [8].

It can be seen from Fig. 2, for example, that Ba is concentrated in the earlier biotites and K-feldspars formed at higher temperatures (to about ten times its clarke value) *, while Rb is concentrated in the same minerals formed at lower temperatures (to about seven times its clarke value). This

---

* This does not refer to the Ba-feldspars, celsian and hyalophane, which have a different origin, but to the feldspars crystallizing from magmas.

s to be expected, inasmuch as, in replacing K, the bivalent Ba strengthens he lattice (unless the accompanying replacement of Si by Al weakens it by greater amount), while Rb, having a larger ionic radius, would weaken it. n augites, hornblendes and biotites, Cr and Li replace Mg or Fe, probably ccording to the scheme $2Cr^{3+} \rightarrow 3Mg^{2+}$ and $2Li^{+} \rightarrow Mg^{2+}$ (more exactly, iAl → 2Mg). In the high temperature generations of these minerals, Cr ontent is higher but diminishes rapidly from augite to biotite. The behavor of lithium is quite the opposite, and it accumulates in the late biotite. This is to be expected, since the entry of Cr increases lattice energy, hile the entry of Li diminishes it. *

Strontium behaves like Ba in the feldspars and replaces Na and K. Like alcium, it is concentrated in the more basic plagioclases (Sr content is 0 times as high as its clarke value), which are relatively early. It is true hat, following Goldschmidt, Nockolds and Mitchell believe that Sr substiutes for Ca; and if so, it behaves contrary to the general rule, being larger nd yet accumulating in the early plagioclases. However, this view, based n the closer similarity in size between Sr^{2+} and Ca^{2+} than between Sr^{2+} nd Na^{+}, although it is generally accepted at present, can hardly be regarded as valid in the case of heterovalent isomorphism** (especially for eldspar lattices, which are far from having closest packing in which NaSi s replaced by CaAl and therefore by SrAl). In any case, if we accept N. V. elov's hypothesis [2] that Ca and Mg are the leading elements in petroenesis and Na is captured merely as an analogue of Ca, the energy comarisons must be made between SrAl and NaSi, and not between SrAl and aAl.

The behavior of Mn with respect to Fe and Mg in augites, hornblendes d biotites is similar. Inasmuch as the ionization potential of Mn^{2+} is ss by only 0.6 e.v., than that of Mg^{2+} and its size is considerably larger y 0.13 A), manganese entering into octahedral coordination will weaken ther than strengthen the lattice, and is more likely, therefore, to become ncentrated in the later, low temperature generations.

The behavior of Sc in paragenetically related augite, hornblende and otite is very instructive. According to V. V. Shcherbina, and this does t contradict the data of Fig. 2, the Sc_2O_3 content in these minerals is 90, and 10 g./ton, respectively. Although, so far as the possibilities of isomorphism are concerned, the biotite lattice, according to Belov's picturesque expression [2], is like a "garbage can," it is almost completely devoid of Sc*. This is explained by the fact that the substitution of $3Mg^{2+}$ by $2Sc^{3+}$ is even more effective than substitution by $2Cr^{3+}$ (because the ionization energy of Sc is noticeably less), and therefore Sc is concentrated in the higher temperature mineral, augite.

---

*This is shown by the following calculations. The ionization energies of ., Mg and Cr are 5.37, 22.73 and 55.23 e.v., respectively. The share of ergy contributed by an ion to the lattice may be estimated from Fersman's ^{3} values [14] by the formula $\underline{K}\frac{w^2}{2r}$. With the radii of these ions being 78 A, 0.78 A and 0.65 A, respectively, and $\underline{K}$ = 11.1 e.v., their energy ares will be 7.1, 28.4 and 76.8 e.v. Hence, from the difference the subitution of $2Cr^{3+}$ for $3Mg^{2+}$ will contribute 26.1 e.v., and substitution of i^{+} for Mg^{2+} will require 2.3 e.v. The actual differences will be less, pecially for Cr^{3+}, because the $\underline{Ek}$ value for multivalent ions is usually wer than $\frac{w^2}{2r}$ (for Cr^{3+}, it is 7.0, but the empirical $\underline{Ek}^{1}$ = 4.75, and even ^{2} = 5.3 cannot be used in such calculations).

*Sr replaces Ca in apatites, but the Sr content in apatites, as is corctly pointed out in [10], is determined also by the factor of its entry into ldspars.

It is known that Sc replacing Fe in wolframite is concentrated in the rare metal deposits of the greisen type formed at the highest temperatures [4].

The valence analogue of scandium, yttrium, has a considerably larger ionic radius (1.06 A) and smaller ionization potential and behaves differently (Fig. 2). It is a heterovalent analogue of Ca.

About the other elements listed in Fig. 2, only a few remarks will be made.

In accordance with theoretical deductions [8], gallium, because of its position in the periodic table (indicating its high electropositivity), is a partial analogue of Al in the tetrahedral coordination, i.e., in essentially covalent structures, but becomes a complete analogue of Al^{3+} in the octahedral coordination. Therefore, Ga is accumulated in muscovite. Small amounts of Ga in the feldspars (2 - 3 times as high as its clarke) may largely be bound in their alteration products (sericite, etc.), and in hornblendes and biotites Ga is apparently held in 6-coordination.

Nickel and cobalt possess considerable bonding properties [8] but are not noticeably concentrated in the primary silicates, where their content may be equal to or considerably lower than the clarke values. A relatively high Ni content in serpentine developed after olivine does not prove, as is usually believed, that it is always present in the olivine lattice [5, 10]. If sulfur is present in the system, Ni may occur in olivine in sulfide inclusions [8].

Vanadium changes its valence very easily; it may be not only trivalent and pentavalent but also bivalent and tetravalent, and for this reason it is very difficult to predict its behavior theoretically. However, it was shown by Shcherbina in a paper presented at the Geochemical Symposium** that in deep-seated processes vanadium is mainly trivalent and accumulates in the early Mg-Fe silicates, such as aegirine, and according to the data of Fig. 2, in some other minerals, including titanomagnetite. In its behavior it closely resembles iron and titanium and apparently replaces Fe^{3+}, for example in titanomagnetite, in the form of $FeO \cdot V_2O_3$ component. This behavior of vanadium is explained by its having intermediate properties

---

*Concentration of Sc in biotites and ferri-muscovites is known when these minerals occur as colored components of acid rocks.

It is interesting to note that in 1953, Oftedal [21] suggested that it might be possible to determine the temperature of formation of biotite, and therefore of the rocks containing it, by its Sc content. However, this proposal ignores a fact known to its author that, in the basic rocks, biotite, as a relatively late mineral, absorbs only the remaining Sc after the bulk of the element has been captured by the earlier minerals (pyroxenes and amphiboles), while in the acid rocks, biotite is essentially the only concentrator of scandium.

**V. V. Shcherbina and L. F. Borisenko. Geochemistry of rare elements in connection with the problem of petrogenesis. Trans. of Geochemical Symposium. Academy of Sciences USSR, 1959.

etween those of the more common elements of the iron group, titanium
nd iron. If the successive ionization potentials of Ti, V and Fe (in e.v.)
re written out:

Ti -- 6.81	13.6	28.39	45.40	101.7	
V -- 6.74	15.13	30.31	48.35	68.7	132.8
Fe -- 7.83	15.9	31.69	55.9	79.0	104.9

is easy to see that in the presence of FeO, VO_2 and V_2O_5 are energeti-
ally at a disadvantage, because oxygen will convert Fe^{2+} into Fe^{3+} by tak-
g an electron from it more easily than V^{3+} and V^{4+} or Ti^{3+}; but with in-
reased concentration of oxygen, Ti^{3+} will be the first to lose its fourth
lectron, or in the absence of Ti, V^{3+}, and then the history of vanadium as
$^{4+}$ will be radically different. If we consider also the influence of bonding
nergy, which depends mainly on the charge and the ionic radii (which are
.83 for Fe^{2+}, 0.67 A for Fe^{3+}, 0.65 A for V^{3+} and 0.64 A for Ti^{4+}), then
becomes clear that Fe and Ti have a stabilizing effect on V^{3+}. Thus, be-
g intimately related to Fe and Ti, V^{3+} must replace Fe^{3+} because, with
e smaller total ionization potential (by 3.2 e.v.) and a slightly smaller
nic radius, this substitution is energetically advantageous. It is this that
uses the accumulation of V both in the relatively early generations of
me silicates and in the titanomagnetites, but not in magnetites and hema-
tes, which do not concentrate vanadium.

4. In connection with what has been said so far, it is necessary to con-
der L. V. Tauson's analysis of Nockolds' and Mitchell's material and of
e rules of isomorphism derived by them [12]. Let us note at the outset
at in analyzing the same rules of isomorphism as presented by Gold-
hmidt and the causes of polar isomorphism formulated by Fersman [14],
auson, applying his law of energetics to the sequence of crystallization of
licates [11], which contradicts the analogous law proposed by Fersman
4], came to a diametrically opposite conclusion concerning the role of
nergy in isomorphism. In reviewing Goldschmidt's rules, Tauson [12]
emarks quite correctly that in heterovalent isomorphism they take into
count only the energy effect of exchange of one ion for another and not the
fect of exchange of the pair of ions compensating for the difference in
arges. He formulates his two rules as follows:

1) "If the replacing element forms a crystal lattice energetically more
lvantageous than the lattice of the pure mineral, then its content in the
ter generations of this mineral will be higher than in the earlier."

2) "If the replacing element forms a crystal lattice energetically less
lvantageous than the lattice of the pure mineral, its content in the later
nerations of this mineral will be lower than in the earlier."

In conformation of these rules, Tauson cites the Nockolds and Mitchell
agram (Fig. 2), but in an abbreviated form, i.e., only for Ba, Sr, Y, Li,
and Mn, and gives calculated lattice energies per one gram-atom of oxy-
n for the following pairs of minerals: anorthite (1450 kcal.) and albite
550 kcal.), orthoclase (1550 kcal.) and celsian (1430 kcal.). According
these values, it appears that the exchange of CaAl for NaSi or of BaAl
r KSi does not increase, but decreases, the lattice energy, and therefore
eakens rather than strengthens the lattice.

This conclusion, like Tauson's law of sequence of crystallization [11],
probably incorrect, if the bonding between Si and Al and oxygen is purely
nic, i.e., if O, Si and Al are O^{2-}, Si^{4+} and Al^{3+}. For in this case it is
cessary to take into account the energy contribution of oxygen due to the

different degree of its polarization. The consideration of this factor in [6, 8] and independently in [8] shows that the energy contribution of O^{2-} is greater in the Si-O-Al link (or Si-O-3Mg), where O^{2-} is strongly polarized than in the S-O-Si link, where O^{2-} is depolarized [6] or contrapolarized [18]. In reality the bonds in the feldspars are half ionic, half covalent, i.e., $O^{-}\downarrow$, $Si^{++}\downarrow\downarrow$ and $Al^{+}\downarrow\downarrow$ [8].

In such a case, replacements take place according to the following schemes:

$$Na^{+}Si^{++\downarrow\downarrow} \text{ by } Ca^{++}Al^{+\downarrow\downarrow}; \quad K^{+}Si^{++\downarrow\downarrow} \text{ by } Ba^{++}Al^{+\downarrow\downarrow}.$$

The energy actually released is the difference between the energy expended in ionization and the energy liberated when the ions come together. Inasmuch as the number of elementary charges and eovalent bonds in these pairs does not change, it may be argued that the energy contribution of each pair will depend to a considerable degree on the energy expended in ionization.

The amount of energy expended in ionization expressed as the sum of ionization potentials in electron volts for the following pairs equals:

$Na^{+}Si^{2+}$	$Ca^{2+}Al^{+}$	Δ	$K^{+}Si^{2+}$	$Ba^{2+}Al^{+}$	Δ
29.52	24.06	5.46	28.75	21.11	7.64
	$Sr^{2+}Al^{+}$			$Pb^{2+}Al^{+}$	
	22.48	7.04		18.22	0.53

The interatomic distance O - Al and the ionic radius of Ca^{2+} are somewhat larger (by 0.06 - 0.1 A) than the distance O - Si and the radius of Na^{+}. Therefore the electrostatic energy of bonding of the pair $Ca^{2+}Al^{+}$ with oxygen is noticeably smaller than of the pair $Na^{+}Si^{2+}$. It is clear from this that because of the similarity in the energy of covalent bonding of $Al\downarrow\downarrow$ and $Si\downarrow\downarrow$ with oxygen, the exchange of CaAl for NaSi or BaAl for KSi will be advantageous from the point of view of energetics if the energy of ionization decreases considerably. This is actually so. A comparison of the data in the light of this proposition [8] explains fully why Ca and especially Sr are concentrated in the high temperature plagioclases and Ba and Sr in the high temperature potash feldspars. Their entry into the lattice increases its energy. On the contrary, Pb^{2+}, in spite of having a smaller ionic radius than Ba^{2+} accumulates in large amounts in the late potash feldspars, and its concentration is near to the clarke value.

Thus, the arguments used by Tauson in proving his rules are not convincing in the case of heterovalent isomorphism.

It remains to review the arguments for isovalent isomorphism. The estimate of the energy involved in this case is simple and should not, it would seem, lead to disagreement. Tauson uses two examples, and both seemingly prove his second rule (see p. 9). These examples are the replacement of Ca^{2+} by Sr^{2+} and of Fe^{2+} by Mn^{2+}.

However, the first example is not convincing for the plagioclases, for according to what has been said above, Sr^{2+} replaces not Ca^{2+} but Na^{+} (and in the K-feldspars, it replaces not Ba^{2+}, of which there is little, but K^{+}). Here Tauson uncritically used the statement of Nockolds and Mitchell.

As for the second example, it is based on a misunderstanding.

Apparently in copying Nockolds' and Mitchell's diagram (Fig. 2), he shifted the lines representing Mn content [12 (Fig. 1)] to the left by one space, so it appears as if the concentration of Mn diminished in the late hornblende and biotite. This is so stated in the text as well. But this is precisely the opposite of Nockolds' and Mitchell's statement given both in the diagram and the text [10]. The concentration of Mn (this has been checked by the English text) in the late generations as compared with the early, does not decrease but increases. Such an obvious error, unfortunately not infrequent in science, is the result of uncritical use of an appealing hypotheses and of a natural desire to prove it at any cost. This points to the inadvertence of the error and the power of hypotheses.

5. Quite recently Tauson published another article [13], where, justly noting the effect of structure of minerals on the phenomenon of isomorphism and using (in a general way) such concepts as electronegativity and ionization potential, which explain well, for example, the diadochy of Ge, he uses essentially the same idea as in the article discussed above, although without actually citing it. It is asserted, for instance, that the substitution of KSi by BaAl is not advantageous from the point of view of energetics. The example taken from [10] of the substitution of Li for Mg, which is especially effective in biotites, is used. It is asserted that the substitution of Li^+Al^{3+} for $2Mg^{2+}$ in pyroxenes must be advantageous, for this is indicated by calculations, and the common occurrence of spodumene, although only in pegmatites. However, this substitution does not occur in pyroxenes in general (Fig. 2), and the reason for this must be sought, says Tauson, in the peculiarities of the chemical bond and especially, as pointed out by Ramberg [17], in the higher electronegativity of the silicate structure of micas (sheets) than of the pyroxenes (chains) and the lower electronegativity of Li as compared with Mg (0.1 and 1.2, respectively).

However, the exchange of Li^+Al^{3+} for $2Mg^{2+}$ is by no means energetically advantageous. Indeed, the expenditure of energy in the ionization of two Mg atoms with $\Sigma \underline{i}^2 = 22.73$ e.v. is 45.46 e.v., i.e. considerably less than the total $\underline{I}$ -- Li = 5.37 e.v. and $\Sigma \underline{i}^3$ Al = 53.14 e.v. or the total of 58.51 e.v. But the main characteristic of Al is its very high $\underline{I}_3$. Therefore, while there are enough alkali metals and alkaline earths in the melt to saturate O to O^-, Al will form essentially covalent bonds and have 4-coordination. Only as the result of decreased concentration of these metals, i.e. with increased acidity of the melt, will Al pass into 6-coordination and become Al^{3+} cation. This behavior of Al is proved experimentally by measuring the electrical conductivity of silicate melts [9]. Moreover, using Ramberg's ideas, this must be done logically. For, if the electronegativity (according to Pauling) of Li is less than of Mg, the electronegativity of Al (1.6) is considerably greater than that of Mg.

It should be noted, in general, that spodumene, as has been pointed out by Betekhtin [3], is not isomorphous with other pyroxenes. The cause of this is its steric peculiarities, i.e., the same cause which prevents isomorphism between biotite and muscovite [2].

The problem of Li-Mg diadochy seems to be easily solved. The replacement of Mg^{2+} by $2Li^+$ by $1/2(Li^+Al^{3+})$ decreases the lattice energy and therefore occurs in the late minerals.

It should be remarked in passing that the data cited in the paper on the distribution of Rb, Ba and Pb in K-feldspar and biotite [13, Table 1] are a direct confirmation of the proposition given in reference [8], if, as the author asserts [13], biotite separates in the final phase of crystallization. By replacing K, Rb weakens the lattice, but Ba strengthens it. Therefore, even independently of the structure of lattices, Rb is mainly concentrated in biotites, and Ba in the earlier feldspar. In accordance with what was said before, K-feldspars do not offer any special advantage towards concentration of Pb^{2+}. Rather, certain advantages may be offered by biotites.

It should be noted that, from the point of view developed here, the striking fact of affinity of rubidium for thallium, on the one hand, and for lithium, on the other, becomes understandable. It is known that Li enrichment in muscovites is accompanied by enrichment in Rb and Tl, and that lithium minerals, zinnwaldite, lepidolite and others, are concentrators of Rb and Tl [1]. It is known also that Li, like Al and Fe, is located in the octahedral layers of micas, while Rb and Tl, with K, are located between the layers. Therefore, there is no direct crystallochemical dependence in the distribution of these elements either on valence or on volume compensation. The only cause of such distribution is energetic. The entry of all of these elements weakens the lattices. During the course of crystallization, these elements are concentrated in the melt and begin to enter the crystal lattices only when temperatures are low and when the weakening of the lattices is of little significance, although the general cause of isomorphism, the energetic advantage of a mixed compound over a separate crystallizing of "pure" compounds relatively similar in composition and energetic properties continues to be in force [8].

6. The above discussion permits a refinement of the rules of isomorphism formulated earlier [14, 15, 8].

The possibility of isomorphism depends on the similarity of properties. These properties may characterize compounds as a whole (similarity of chemical composition, lattice structure or energy characteristics) or of individual elements (similarity of chemical bonding, size of atoms and ions, etc.).

The cause of isomorphism, insofar as it is determined (like the formation of "pure" compounds) by the laws of thermodynamics, is a slight energetic advantage of formation (exothermic process) of crystalline compounds of mixed composition over formation (especially by rare elements) of independent compounds. The formation of mixed compounds indicates, moreover, a greater disorder, a higher entropy of distribution of matter.

Superimposed upon this general cause, in different geological processes, there are additional or particular causes and conditions. The most important of these is the capacity of some replacing elements to increase lattice energy, to strengthen the lattice, and of others, to decrease lattice energy and weaken the lattice. It is precisely these causes that determine the behavior of admixed elements in crystallizing magma.

During the early, relatively high temperature stages of crystallization, only those elements enter diadochically into crystal lattices in amounts exceeding their concentration in the crystallizing system which are capable of strengthening the lattices. These elements are captured (it is possible that the crystallization of compounds with such admixtures occurs a little earlier).

In the succeeding relatively low temperature stages of crystallization, when the concentration of the elements which are not being captured by the lattices increases, they may enter into the lattices even though they decrease lattice energy. These elements are admitted.

These two phenomena, whose prediction is more difficult than suggested by Goldschmidt's rules of diadochy, which take only the charge and size of the ions into consideration and not their ionization potentials, the role of coordination number (in heterovalent substitutions) and the character of ponding complicate the pattern of distribution of rare as well as relatively abundant elements against the background of the general cause of somorphism.

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EOCHEMISTRY OF THALLIUM AND RUBIDIUM IN IGNEOUS ROCKS

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(ABSTRACT)

The study and the analysis of the Rb/Tl ratio for rocks of the young agmatic hearth of Tyrny-Auz as well as for ancient rocks of this region onfirm the geological conclusions of a common magmatic source for young trusive and effusive rocks of Tyrny-Auz and establish the difference of ese rocks and the ancient rocks of the Chief mountain range.

The strong fluctuations of the Rb/Tl ratio in some samples of leucocratic ranitoids from 60 to 340 as well as the analogous fluctuations of this ratio the contact-altered varieties of biotitic granite allow to advance the as- umption on the difference in the conditions of the formation of the leuco- ratic and biotitic granites. Some decrease in the Rb/Tl ratio in leuco- ratic granitoids and in the nearby-contact parts of the biotitic granite ompared to normal biotitic granite) bears witness of the enrichment of e latter in thallium compared to rubidium. For the contact-altered gran- e this enrichment is conditioned by the removal of thallium from the cen- r of the intrusive to the endocontact.

The difference in the character of the thallium and rubidium bond in sili- tes as well as the high volatility of the haloid thallium compounds lead to e separation of rubidium and thallium and, hence, to the disturbance of nstancy of the Rb/Tl ratio in rocks which are products of assimilation, bridism or were subjected to hydrothermal action connected with the etasomatic alteration of potassium minerals.

There are several works devoted to the geochemistry of thallium and ıbidium in igneous rocks [1-9]. Thanks to these investigations, the main atures of the behavior of thallium and rubidium during the magmatic proc- s have been clarified. It has been shown that during fractional crystalli- tion the univalent thallium and rubidium having large ionic radii and low arges accumulate in the later, acid differentiates of magma. This, in V. Tauson's opinion [8, 9], makes these elements useful in refining age relationships among genetically related series of rocks.

It seems to the author that this characteristic of thallium and rubidium is likely to be of rather limited use, mainly because one very often deals with rocks altered by postmagmatic processes which undoubtedly mask the primary pattern of distribution of these elements, or with hybrid rocks in which any sharp regularity in the distribution of the elements can hardly be expected.

For the same reasons, the Rb/Tl ratio proposed by Ahrens [2, 4] as a geochemical index of genetic relationship in igneous rocks is not constant.

In Ahrens' opinion, the close geochemical affinity of thallium and rubidium is due 1) to the very similar chemical properties of univalent minerals and 2) to the identical ionic radii of rubidium and thallium (1.49A), which are near in size to the ionic radius of potassium (1.33A). Evidently rubidium and thallium may enter with equal ease into potassium minerals, and this explains why almost the entire mass of thallium and rubidium in the earth's crust is concentrated in these minerals.

Inasmuch as rubidium and thallium have lower ionization potentials and weaker electrostatic forces than potassium, they accumulate in the rest magmas and are concentrated in the final products of differentiation.

As can be seen from the above, Ahrens considered only the similarities between the properties of rubidium and thallium. But there are also differences in the properties of these two elements which may and do cause separation of rubidium and thallium during some processes and, therefore, destroy the constancy of the Rb/Tl ratio. It will suffice to mention the difference in the character of bonding of rubidium and thallium in the silicates, due to the greater tendency of thallium to form covalent bonds and the greater volatility of thallium compounds, especially of the halides.

The author encountered a case in which the Rb/Tl ratio did not remain constant, in analyzing this ratio in the young granitic rocks of Tyrny-Auz (Northern Caucasus).

According to several investigators the activity of the young magmatic hearth of Tyrny-Auz comprised three stages, resulting in the intrusion of 1) leucocratic granitic rocks, 2) porphyritic biotite granites and 3) rhyolitic dikes and stocks [14, 16].

The dikes and stocks of leucocratic granitic rocks are enclosed by marbles and biotite hornfelses. A. V. Pek [10] believes that these rocks were metamorphosed by the intrusion of biotite granites before the intrusion of leucocratic granitic rocks, but does not exclude the possibility that the latter are apophyses of the biotite granite.

The leucocratic granitic rocks are not uniform but include a series of rocks, the most widespread being: 1) granite porphyries, 2) granitic aplites and 3) labradorite aplites. All these varieties contain quartz, anorthoclase, plagioclase, and small amounts of biotite. In the granitic aplites replacement of the acid plagioclase by labradorite and concomitant silicification are sometimes observed. The labradorite aplite is composed of labradorite (up to 80%), quartz, and a little biotite.

The biotite in the leucocratic granites is strongly chloritized, indicating hydrothermal alteration of the rocks. L. A. Vardanyants [12] considers the granitic rocks as the products of a sequence of magmatic intrusions of different composition, while V. V. Lyakhovich [11] and A. V. Pek [10] ascribe the variation among them to the different degree of assimilation of the country rock and to variation in the physicochemical conditions of crystallization of a single magma.

The porphyritic biotite granites (El'dzhurtinskii) are uniform in composition (quartz, anorthoclase, plagioclase, biotite) and are rather widespread. In some areas these granites are bleached at the contacts with marble and very closely resemble the leucocratic granitic rocks.

The rhyolites occur in dikes and in three small massifs. Vardanyants [12] believes that they include rocks of different ages. The altered rhyolite of the dikes and of the middle massif, he refers to the Upper and Middle Pliocene, and the rhyolites of the northern and southern massifs, to the Upper Pliocene. V. V. Lyakhovich thinks that the rhyolites are all of the same age and ascribes the more intensive alteration of the middle massif to its greater exposure.

The groundmass of the rhyolites is composed of quartz, potassium feldspar (sanidine), and biotite; the phenocrysts are quartz, sanidine, plagioclase, and biotite.

In addition to these rocks, S. P. Solov'ev described a thin vitrophyre dike which he believes to be younger than the rhyolites [13]. According to him, the rhyolites were intruded soon after the emplacement of the granites, possibly from the same magma chamber. In favor of this view are the similarity of chemical and mineralogical composition of the granites and rhyolites and the similarity of attitude.

The contact metamorphism caused by the young intrusives was accompanied by the introduction of a large number of elements, and by the removal of some. In many areas, different contact metamorphic phases were superimposed [13]. These complex processes resulted in the formation of skarns.

In spite of the numerous investigations of the young intrusives of the Tyrny-Auz region, the genetic relationship between the El'dzhurtinskii granites and the leucocratic granitic rocks remains obscure and debatable. . D. Afanas'ev [14] believes that a detailed petrographic and geochemical study is needed to solve this problem.

The data on the relative and absolute ages of the granites are also uncertain. Afanas'ev [14] leaves open the question "whether the rhyolites are the late differentiates of the same magma which produced the granites or whether they represent the beginning of new volcanic activity."

Inasmuch as the analysis of closely related pairs of elements and especially of rubidium and thallium may throw light on some of the genetic problems, the author investigated the distribution of rubidium and thallium in these rocks and in their minerals. Thallium was determined colorimetrically with brilliant green [15], and rubidium by flame photometry.

The results of these determinations are given in Table 1.

As the table shows, the thallium and rubidium content in the young granitic rocks of Tyrny-Auz increases from the leucocratic to the biotite granites, and in the hypabyssal rocks, from the rhyolites to the vitrophyres. The strong impoverishment (5 to 10 times) of the leucocratic rocks in thallium and rubidium as compared with the biotite granites and rhyolites is striking, especially as these rocks differ little in the alkali and particularly in the potassium content (Table 2).

Samples 047 and 048 are exceptional in being enriched in rubidium and thallium, and they carry small amounts of biotite, which is a concentrator of these elements.

There is little difference in the thallium and rubidium content among the varieties of leucocratic granitic rocks, but the labradorite aplites, which contain little potassium, have the lowest content of these elements.

In the porphyritic biotite granites, thallium and rubidium are rather uniformly distributed, except for the bleached varieties of granite (at contacts),

Table 1

Sample No.	Description of rocks	Tl, %	Rb, %	Rb/Tl
Leucocratic granitic rocks				
016	Granite porphyry	$3 \cdot 10^{-5}$	$3.5 \cdot 10^{-3}$	120
023	"	$3 \cdot 10^{-5}$	$3.5 \cdot 10^{-3}$	100
027	"	$2 \cdot 10^{-5}$	$2.3 \cdot 10^{-3}$	115
038	"	$4 \cdot 10^{-5}$	$4.5 \cdot 10^{-3}$	110
039	"	$2 \cdot 10^{-5}$	$1.2 \cdot 10^{-3}$	60
050	Granite porphyry	$2 \cdot 10^{-5}$	$1.4 \cdot 10^{-3}$	70
031	Granite aplite	$3 \cdot 10^{-5}$	$3.0 \cdot 10^{-3}$	100
024	Variety transitional between granite porphyry and labradorite aplite	$1 \cdot 10^{-5}$		
040	"	$3 \cdot 10^{-5}$		
025	Labradorite aplite at contact with marble	$1 \cdot 10^{-5}$	$1.0 \cdot 10^{-3}$	100
033	Labradorite aplite	$2 \cdot 10^{-5}$	$2.4 \cdot 10^{-3}$	120
034	"	$3 \cdot 10^{-5}$	$4.5 \cdot 10^{-3}$	150
T-10	"	$1 \cdot 10^{-5}$	$0.75 \cdot 10^{-3}$	75
	Average	$2.3 \cdot 10^{-5}$	$2.5 \cdot 10^{-3}$	107
047	Hydrothermally altered granite porphyry	$6 \cdot 10^{-5}$	$10.5 \cdot 10^{-3}$	175
048	"	$12 \cdot 10^{-5}$	$41.0 \cdot 10^{-3}$	340
Porphyritic biotite granites (El'dzhurtinskii). Unaltered				
01	Drill hole 41, depth 1982 m	$1.1 \cdot 10^{-4}$		
02	" 2003 m	$1.2 \cdot 10^{-4}$	$1.95 \cdot 10^{-2}$	162
03	" 2020 m	$1.2 \cdot 10^{-4}$	$1.5 \cdot 10^{-2}$	125
05	From the surface	$1.3 \cdot 10^{-4}$	$1.5 \cdot 10^{-2}$	115
07	"	$1.2 \cdot 10^{-4}$	$1.4 \cdot 10^{-2}$	116
010	From the surface along the central fault	$1.0 \cdot 10^{-4}$	$1.2 \cdot 10^{-2}$	120
011	"	$1.5 \cdot 10^{-4}$	$2.1 \cdot 10^{-2}$	140
013	"	$1.3 \cdot 10^{-4}$	$1.65 \cdot 10^{-2}$	127
015	"	$1.7 \cdot 10^{-4}$	$2.2 \cdot 10^{-2}$	130
069	From the surface along Chil'miyan gully	$0.9 \cdot 10^{-4}$		
070	"	$1.0 \cdot 10^{-4}$		
073	"	$1.0 \cdot 10^{-4}$	$1.1 \cdot 10^{-2}$	123
075	"	$1.0 \cdot 10^{-4}$	$1.25 \cdot 10^{-2}$	125
076	"	$1.5 \cdot 10^{-4}$		
T-11	From "Zmeika" drift at contact with biotite hornfelses	$1.8 \cdot 10^{-4}$	$2.62 \cdot 10^{-2}$	140
	Average	$1.25 \cdot 10^{-4}$	$1.68 \cdot 10^{-2}$	134

TABLE 1 (Continued)

Sample No.	Description of rocks	Tl, %	Rb, %	Rb/Tl
	Contact metamorphic			
058	Drill hole 34, 2 m from contact with metamorphosed limestone	1.0 · 10^{-5}		
T-9	Bleached rock from contact with marbles	3.0 · 10^{-5}	0.5 · 10^{-2}	167
060	Drill hole 35, at contact with biotite hornfelses	3.0 · 10^{-5}	0.4 · 10^{-2}	133
064	Drill hole 35. Bleached rock	5.0 · 10^{-5}		
067	Drill hole 38. Bleached rock	6.0 · 10^{-5}		
P-721	Bleached rock at contact with marbles	2.0 · 10^{-5}	0.14 · 10^{-2}	70
P-722	"	2.0 · 10^{-5}	0.13 · 10^{-2}	65
P-707	Bleached rock from a dike in the marbles	5.0 · 10^{-5}	0.25 · 10^{-2}	50
	Average	3.4 · 10^{-5}	2.84 · 10^{-3}	84
	Rhyolites			
T-222	Northern massif at contact with biotite hornfelses	1.5 · 10^{-4}	1.7 · 10^{-2}	114
T-223	Northern massif, surface of the central part	1.5 · 10^{-4}	1.5 · 10^{-2}	100
T-224	"	1.5 · 10^{-4}	1.6 · 10^{-2}	100
T-225	"	1.7 · 10^{-4}	1.9 · 10^{-2}	112
T-227	"	1.7 · 10^{-4}	1.7 · 10^{-2}	100
T-228	"	1.4 · 10^{-4}	1.6 · 10^{-2}	114
B-28	Middle massif, at depth	1.1 · 10^{-4}	1.6 · 10^{-2}	146
	Average	1.6 · 10^{-4}	1.7 · 10^{-2}	106
T-18	Vitrophyre	2.2 · 10^{-4}	2.2 · 10^{-2}	100
	Minerals from biotite granites			
02	Biotite	5.0 · 10^{-4}	6.5 · 10^{-2}	130
02	Feldspar	2.0 · 10^{-4}	2.4 · 10^{-2}	120
B-26	Biotite	6.0 · 10^{-4}	6.0 · 10^{-2}	100
060	Chloritized biotite	6.0 · 10^{-5}	not deter.	
5	Biotite	7.2 · 10^{-4}	8.0 · 10^{-2}	110
5	Feldspar	2.4 · 10^{-4}	3.2 · 10^{-2}	133
015	Biotite	6.0 · 10^{-4}	7.0 · 10^{-2}	117

Table 2

Average Chemical Composition of the Young Igneous Rocks of Tyrny-Auz (%)

Oxides	Granite porphyries*	Granitic aplites*	Labradorite aplites*	Porphyritic biotite granites*	Rhyolites**		Vitrophyre***
					I	II	
SiO_2	75,92	71,32	78,13	72,58	71,34	69,07	64,71
TiO_2	0,04	0,04	0,03	0,35	0,40	0,54	0,35
Al_2O_3	13,45	13,37	13,47	14,11	15,22	14,60	13,17
Fe_2O_3	0,23	0,33	0,15	0,57	0,85	1,01	0,62
FeO	0,34	0,22	1,13	1,53	1,86	1,80	1,53
MnO	0,03	0,03	Traces	0,04	0,02	0,02	0,06
MgO	Traces	0,03	Traces	0,65	0,84	1,05	0,57
CaO	0,74	2,59	4,06	1,72	0,73	2,01	3,44
Na O	3,91	3,06	3,07	3,17	4,80	2,89	1,32
K_2O	4,90	3,34	0,41	4,37	2,09	4,17	2,55
Tl	$2,7 \cdot 10^{-5}$	$3,0 \cdot 10^{-5}$	$2,0 \cdot 10^{-5}$	$1,25 \cdot 10^{-4}$	$1,6 \cdot 10^{-4}$		$2,2 \cdot 10^{-4}$
Rb	$2,7 \cdot 10^{-3}$	$3,0 . 10^{-3}$	$2,16 \cdot 10^{-3}$	$1,68 \cdot 10^{-2}$	$1,7 \cdot 10^{-2}$		$2,2 \cdot 10^{-2}$

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*After Z. V. Studenikova [16]; **After S. P. Solov'ev [13]; ***After L. A. Vardanyants [12]

Note: Comma represents decimal point.

which are very similar to leucocratic granitic rocks both in appearance and n the content of rare elements. Only the rhyolites have a uniform thallium and rubidium content, which is somewhat higher than in the biotite granites. Still richer in these elements are the vitrophyres. Unfortunately, only one sample of vitrophyre was available to the author, and it is impossible, herefore, to give the average rubidium and thallium content in this rock.

If it is assumed that the leucocratic granites are the oldest rocks and hat all the rocks had the same magmatic source, then, in the series: eucocratic granitic rocks--biotite granites--rhyolites--vitrophyres, there s a regular increase in rubidium and thallium content, i.e., from the arliest to the latest products of the magmatic hearth. However, this regu-arity is in sharp contradiction to the other regular tendency of thallium and ubidium to follow potassium during the magmatic process and to gain on it owards the end. If the behavior of potassium in the rocks from the leuco-ratic granitic rocks to the rhyolites is examined, then no great affinity be-ween potassium and thallium and rubidium is discernible in the leucocratic ranitic rocks. One gets the impression that the leucocratic granitic rocks, n the course of their formation, have lost a part of their volatiles, includ-ng thallium and rubidium. The same is true of the altered biotite granites rom the endocontact zone, which also have lost the larger part of these lements.

Table 3 illustrates the difference in the behavior of thallium and rubidium uring contact metamorphism of biotite granite. It shows that thallium is

Table 3

Rock	Tl, %	Rb, %	Rb/Tl
Limestone	$0.40 \cdot 10^{-4}$	$1.0 \cdot 10^{-4}$	2.5
Marble	$0.34 \cdot 10^{-4}$	none	very small
Granite at limestone contact	$0.7 \cdot 10^{-4}$	$6.25 \cdot 10^{-4}$	9
Granite at 1-2 m from contact	$0.9 \cdot 10^{-4}$	$2.5 \cdot 10^{-3}$	28
Granite at 5-6 m from contact	$0.9 \cdot 10^{-4}$	$7.5 \cdot 10^{-3}$	83
Granite at 50-70 m from contact	$1.55 \cdot 10^{-4}$	$1.56 \cdot 10^{-2}$	100

rried out more intensively from the central parts of the intrusive to the docontact and into the invaded rocks than is rubidium. This is indicated the gradual change in the Rb/Tl ratio from 2.5 in the limestones to 100 normal granite far from the contact. It is interesting that, thanks to this igration of thallium, the invaded limestones become enriched in it, where-normal limestones, as was shown by Shaw [7], are completely devoid of allium.

The invaded rocks of Tyrny-Auz, especially the limestones, contain a ole series of elements introduced by the granitic intrusions. It is logical assume, therefore, that the enrichment in thallium is also due to its roduction from the magma. The character of distribution of thallium in granite itself, from the center to the periphery, differs from that of oidium and suggests that thallium migrated as a halide, most likely as a fluoride, and that at the contact, granite crystallized under higher vapor pressure of thallium as compared with rubidium and thus became relatively enriched in thallium.

Thus, the low Rb/Tl ratio in the invaded rocks and at the granite contacts, as compared with this ratio in the Ryrny-Auz granites in general, is explained by the greater volatility of thallium fluoride (Table 7). This explanation does not, of course, exclude other interpretations of the peculiarity of behavior of thallium and rubidium during contact reactions between the magma and the invaded rocks.

In examining the data in the last column of Table 1, we see that in this case the leucocratic granitic rocks differ from the other rocks by inconstancy of the Rb/Tl ratio, which varies widely from 60 to 340. Approximately similar variations are found in the altered varieties of the biotite granite (Tables 2 and 3), while in the unaltered granites and in the rhyolites the Rb/Tl remains constant within the limits of experimental error.

The sharp fluctuations in the Rb/Tl ratio in the leucocratic granitic rocks indicate that these rocks are not uniform and that the conditions of their formation were different from those of the biotite granites.

The variation of the Rb/Tl ratio in the leucocratic granitic rocks may be explained as in the case of biotite granites (Table 3) by the different distance of the investigated samples from the limestone contacts. Macroscopically the samples may well be alike.

The same variations in the Rb/Tl ratio for rocks which are macroscopically almost alike were observed by the author in the study of the distribution of potassium, rubidium, and thallium in quartz albitophyre from the region of the Kvaisinsk lead-zinc deposit. *

This rock has a well developed porphyritic texture. The phenocrysts are plagioclase (albite), potassium feldspar, and quartz. In sample II, albite is strongly sericitized, the phenocrystic potassium feldspar is almost wholly replaced by albite, and biotite, which is completely absent from sample I, appears in the groundmass together with quartz. The determination of K, Rb, and Tl in these samples gave the results listed in Table 4.

Table 4

Sample	K, %	Rb, %	Tl, %	Rb/Tl	K/Rb	K/Tl · 10^2
I	2.7	0.050	0.00012	420	540	225
II	1.97	0.047	0.00007	670	420	280

Table 4 shows that in the process of hydrothermal alteration (sample II) accompanied by sericitization and albitization, together with the removal of

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* The chemical analyses and descriptions of these rocks were done by L. N. Soboleva.

potassium, thallium was also removed and more intensively than rubidium. Because of this, the Rb/Tl ratio in the altered sample increased from 420 to 670.

It is very probable that an analogous process of hydrothermal alteration explains the increase in the Rb/Tl ratio in samples 047 (175) and 048 (340) of the leucocratic granitic rocks of Tyrny-Auz, which, as has already been mentioned, are enriched in rubidium and thallium as compared with other samples, because of the presence of biotite. Of the two samples, 048 is more altered (chloritized) than 047 and its Rb/Tl ratio is twice as high.

This effect of the hydrothermal alteration of rocks on the Rb/Tl ratio is noted by Ahrens [4], who describes a phlogopite and a phlogopite changed to vermiculite from the Palabora syenite. The alteration to vermiculite was accompanied by a more intensive removal of thallium than rubidium (Table 5).

Table 5

Mineral	Rb_2O, %	Tl_2O, %	Rb_2O/Tl_2O
Phlogopite	0.072	0.00020	360
"	0.055	0.00012	420
Phlogopite altered to vermiculite	0.050	<0.0001	>500
"	0.036	<0.0001	>360
"	0.012	none	very large

It follows from what has been said that the constancy of the Rb/Tl ratio is destroyed by the hydrothermal alteration of potassium minerals.

The variations in the Rb/Tl ratio in leucocratic granitic rocks can also be explained by the repeated action of hydrothermal solutions carrying different amounts of thallium and rubidium. In dealing with such complex rocks as the leucocratic granitic rocks, it is difficult to point out the cause of variation in the Rb/Tl ratio.

Comparing the Rb/Tl ratios in the younger rocks with those in the old granitic rocks of Baksan (Table 6), we see sharp and regular differences,

Table 6

Sample No.	Rocks	Tl, %	Rb, %	Rb/Tl
B-4	Microcline biotite granites	$0.80 \cdot 10^{-4}$	$2.30 \cdot 10^{-2}$	290
B-5	" "	$0.75 \cdot 10^{-4}$	$2.00 \cdot 10^{-2}$	270
M-5	Two-mica granites	$1.10 \cdot 10^{-4}$	$1.75 \cdot 10^{-2}$	160
M-6	"	$1.30 \cdot 10^{-4}$	$2.10 \cdot 10^{-2}$	160
M-7	"	$0.90 \cdot 10^{-4}$	$1.00 \cdot 10^{-2}$	110
M-8	"	$1.00 \cdot 10^{-4}$	$1.60 \cdot 10^{-2}$	160

and this points once more to the genetic relationship among the young igneous rocks and to the different mode of formation as compared with the old rocks of the Main Range exposed in the southwestern part of the Tyrny-Auz region.

The constancy of the Rb/Tl ratio (within the limits of experimental error) in the young intrusive and hypabyssal rocks of Tyrny-Auz gives the investigators of igneous activity in this region additional data for judging which of the rocks are comagmatic.

The author, however, became interested in something else that was disclosed by this investigation, namely, by the difference in the behavior of thallium and rubidium in a number of processes.

The data on the effect of hydrothermal activity on the value of the Rb/Tl ratio obtained by various investigators lead to a very interesting conclusion concerning the difference in the mobility of thallium and rubidium during the process of replacement of potassium minerals. In the sericitization and albitization of potassium feldspar in quartz albitophyre, chloritization of biotite in leucocratic granite porphyry (samples 947 and 048), and in the alteration of phlogopite into vermiculite, thallium exhibits greater mobility than rubidium. To this should be added the case of greater mobility of thallium during the reaction between biotite granite and the invaded limestones.

The cause of this difference in the mobility of thallium and rubidium must be sought in the character of bonding of these elements in the silicates. Thallium, with its 18-electron shell, has a greater tendency towards covalent bonding with oxygen in the silicates than rubidium, because the electronegativities of thallium and rubidium (according to A. S. Povarennykh [17]) are 140 and 97, respectively. Hence the energy of the rubidium-oxygen bond is greater than that of the thallium-oxygen bond, and the latter is more easily expelled from the lattice of potassium minerals than rubidium. The difference in the behavior of thallium and rubidium during the contact reactions between granite and limestone, i.e., the greater mobility of thallium, the author tends to ascribe to the much greater volatility of thallium halides (Table 7).

Table 7

Volatility of Thallium and Rubidium Halides

Rubidium halides	Boiling temperature °C	Thallium halides	Boiling temperature °C
RbF	1410	TlF	655
RbCl	1381	TlCl	806
RbBr	1352	TlBr	819
RbI	1305	TlI	823

Similar variations in the Rb/Tl ratio were observed by L. N. Kogarko [18] in the granitic rocks of the Turgoyak massif. The decrease in the Rb/Tl ratio from leucocratic granites (230) to biotite granites (180) and ranodiorites (80) she explained by a more intensive removal of thallium rom the central to the peripheral parts of the massif during the formation f these rocks by hybridization from the initial leucocratic granite magma.

An analysis of the observed facts of variation of the Rb/Tl ratio in the enetically related igneous rocks suggests that the basic processes reponsible for them are: 1) the deuteric alteration of the rocks by postagmatic processes and 2) the hybridization of the magma accompanied by n intensive removal of the alkalies.

In brief, the variations in the Rb/Tl ratio in the comagmatic rock series nvestigated by different authors are due to the fact that these rocks are not ure products of differentiation of a juvenile magma in which rubidium and hallium enter on equal terms into the lattices of potassium minerals, acumulate towards the end of the magmatic process, and enrich the rest agma.

In some cases these rocks are hybrids which had lost their alkalies in e gas phases; in other cases they had undergone alteration by hydrotheral solutions either related or unrelated to the given magmatic hearth. hese processes, naturally, are not the only ones which cause separation thallium and rubidium during the magmatic cycle. Further study is eeded for the solution of this interesting problem in the geochemistry of bidium and thallium.

In connection with these facts it is appropriate to make a few remarks oncerning Shaw's statement [7] that there is a substantial difference in the b/Tl ratio in gabbros and basalts (138), granites (268), and pegmatites 95).

It seems to the author that the figures obtained by Shaw for gabbros and salts are more or less accidental, for he calculated the average ratio rom 10 analyses, while his average for pegmatites was based on 140 anales of mineral samples made by Ahrens [4]. Considering that the thallium d rubidium content in gabbros and basalts is near the limit of sensitivity the analytical method, the validity of the average based on ten analyses more than doubtful. Therefore, the difference in the Rb/Tl ratio in gabos (138) and pegmatites (95) may be disregarded.

As for granites, the reason for their high Rb/Tl ratio (268) must be ught in the nature of the granites themselves. As has already been rearked, the hydrothermal alteration of granites plus their hybrid origin sult in a definite separation of thallium and rubidium by the preferential moval of the former into the invaded rocks and hydrothermal products, d therefore in an increase in the Rb/Tl ratio.

In the granites which are neither hybrid nor altered, the Rb/Tl ratio ould approach an average which is probably not far from 100 and is ually characteristic of other igneous rocks.

In summarizing the peculiarities of behavior of thallium and rubidium ring the magmatic process, it is necessary to point out once more the rong affinity between thallium and rubidium during the fractional crystalation of the magma and the possibility of their separation and hence of olation of the constancy of the Rb/Tl ratio in genetically related rocks unr the influence of a number of different processes.

It is apparent that the use of the Rb/Tl ratio as a geochemical index of netic relationship of igneous rocks is possible only in combination with a dy of the behavior of essential elements and a detailed petrographic alysis.

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GALLIUM IN THE ALKALIC ROCKS OF THE SANDYK MOUNTAINS MASSIF (NORTHERN KIRGIZIYA)

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(ABSTRACT)

The gallium distribution over various alkaline rocks of the complex massif and in some minerals has been studied. It is stated that the average Ga-content in the massif is $19 \times 10^{-4}\%$ of Ga and that the Ga/Al ratio insignificantly deviates from the average value of 1.9×10^{-4}. In the course of the intrusion development some Ga-accumulation from the first stages (alkaline gabbroids and alkaline-earth syenites) to the final (nepheline syenites) is observed; this is in conformity with the Al increase in the same direction. The vein rocks are enriched in Ga compared to the intrusive rocks. Higher Ga-concentrations are detected in biotites and hornblende compared to earlier orthoclases and nepheline. This is discussed from a crystallochemical standpoint and taking into consideration the crystallization order of the rock minerals.

The distribution of the typical "dispersed" element, gallium, in igneous rocks has been rather thoroughly studied by a number of investigators. This is especially true of the more common acid, intermediate, and basic rocks. The intimate geochemical relationship between Ga and Al and its lithophile character of behavior in magmatic processes are well established. Relatively recently, D. M. Shaw [1] published a summary of the geochemistry of gallium with extensive data for different igneous rocks and minerals.

The data for the alkalic rocks are very few, and especially the data for the distribution of Ga in rocks genetically related to a single source. R. A. Higazy's investigations in Southwest Uganda (Africa) deal with uncommon mafic volcanic rocks [2]. The data for the common alkalic rocks are few and scattered. But in spite of the scarcity of quantitative data, Shaw remarks that V. M. Goldschmidt's idea [3] of high gallium concentrations in alkalic rocks as compared with other igneous rocks is not completely confirmed. In the present paper the authors discuss the behavior of Ga during the crystallization and differentiation of alkalic magma, using the complexely differentiated Sandyk Mountains massif as an example. Some of the dikes related to this pluton also were analyzed for gallium.

Altogether, 50 rock samples, including average samples (mixed), and 11 minerals were analyzed.

Gallium in rocks and minerals was determined spectrographically by the method worked out by L. A. Borisenok [4]*.

The Sandyk Mountains alkalic massif is located in the Caledonide zone of Northern Tien Shan, on the watershed of the Dzhumgol-Tau Range, and is the product of Variscan magmatism. The alkalic magma, near in composition to the average calcic syenite type, was intruded along a fault zone in the ancient basement and formed a complex two-phase pluton. The sequence of intrusions appears to have been as follows (from earliest to latest): first phase, a) alkalic gabbroids (monzonites, monzonite-essexites, and monzonite-shonkinites); b) porphyritic calcic syenites with pyroxene and biotite (these are the most widespread rocks); and c) leucocratic calcic syenites; second phase, d) hornblende alkalic syenites and e) nepheline syenites of the miaskite type (mainly biotite-augite rocks). The approximate areas of exposure of the main types of these rocks are listed in Table 2. The mineralogy of the representative rock types is given in Table 1.

More detailed information on the petrography and structure of the massif will be found elsewhere [5, 6].

Distribution of gallium during the crystallization of the alkalic rocks of the Sandyk Mountains massif.

The discussion of the distribution of gallium during the crystallization of the alkalic rocks of the massif will be based on the study of three most characteristic representatives of these rocks: the porphyritic alkalic syenites of phase I (sp. 265), the hornblende calcic syenites of phase II (sp. 1147) and the nepheline syenite of phase II (sp. 268). In all three samples, Ga was determined in the essential rock-forming minerals: orthoclase, pyroxene, biotite, hornblende, and nepheline. The plagioclase was excluded because it was found impossible to separate it completely from orthoclase (in sample 265). In the other two samples, plagioclase occurs in negligible amounts (sp. 1147) or is not present (sp. 268).

Micrometric analyses were made on large 8 x 10 cm thin sections.

The results of analyses for gallium are given in Table 1. They show that biotite has the highest Ga content (in p.p.m.) (30, 71 and 65) and orthoclase the lowest (17, 13 and 14). The nepheline from nepheline syenite is also rather poor in gallium (34 p.p.m. Ga).

In the plagioclase from sample 265, the content of Ga evidently does not exceed 17 p.p.m. Ga, since the analysis of the total feldspar (orthoclase + plagioclase) gave 17 p.p.m. Ga, i.e., the same figure as for orthoclase alone. A relatively high Ga content--55 p.p.m. Ga--was found in hornblende, although it contains only 5% Al**. The augite from nepheline

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*The sensitivity of the method is 1 p.p.m. Ga, and the average analytical error, ± 10%.

**According to semiquantitative spectrographic analysis.

Table 1

Distribution of Ga among Minerals in the Main Types of Alkalic Rocks of the Sandyk Mountains Massif

Minerals	Percentage of mineral in the rock	Gallium content in mineral p.p.m.	Share of Ga in the rock carried by a given mineral	
			g/ton	weight (amount in rock = 100)
Sample 265. Porphyritic calcic syenite. Phase I (19 p.p.m. Ga)				
Orthoclase	68.1	17	11.6	61.0
Plagioclase	7.9	n.d.	—	—
Pyroxene	15.0	13	1.9	10.0
Biotite	7.1	30	2.1	11.0
Total	98.1		15.6	82.0
Sample 1147. Hornblende alkalic syenite. Phase II (14 p.p.m. Ga)				
Orthoclase perthite	87.9	13	11.4	81.4
Plagioclase	0.81	n.d.	—	—
Hornblende	9.9	55	5.4	38.5
Biotite	0.22	71	0.1	0.7
Total	98.83		16.9	120.6
Sample 268. Nepheline syenite. Phase II (19 p.p.m. Ga)				
Orthoclase	75.0	13	10.5	55.2
Nepheline	15.6	34	5.3	28.0
Biotite	4.3	65	2.8	14.6
Augite	1.3	23	0.3	1.5
Total	96.2		18.9	99.3

syenite contains 23 p.p.m. Ga with Al content of about 5%*, and the augite from the calcic syenite contains only 13 p.p.m. Ga with Al content of 2%*. It would appear that the gallium content in the pyroxenes may be correlated with their alumina content.

However, the concentration of Ga in the rock-forming minerals cannot be explained completely on the basis of the distribution of Al among them.

The minerals richest in alumina (orthoclase and nepheline) contain much less Ga than the less aluminous biotites and hornblendes. The reason for such distribution of Ga may be the condition of crystallization of the rocks (the order of crystallization of the minerals and their relative amounts during the process) and the nature of bonding and position of Ga in the mineral lattices in relation to the replaced aluminum.

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*According to semiquantitative spectrographic analysis.

For example, it is not difficult to see that the Ga content in minerals is, in general, inversely proportional to the content of these minerals in the rock. This conclusion is permissible because in all three samples the total amount of gallium is approximately the same and the identical minerals are found but their amounts in the rocks differ (for example, biotites and pyroxenes). The examination of the large thin sections shows that the large idiomorphic crystals of orthoclase were the first to crystallize. Constituting the bulk of the material in all three rocks, orthoclase "captured" in its lattice not the concentrated Ga of the late magmatic stages but Ga which, together with Al, was dispersed throughout the full volume of the melt. This is confirmed by the fact that the Ga content in the orthoclase is near the total Ga content in the rock. The amount of Ga in the orthoclase ranges from 61 to 81% of the total Ga in the rock.

The biotite in the investigated rocks was the latest mineral to crystallize, and it occurs in thin plates squeezed in between prismatic feldspar crystals. In the biotites, Ga is not a mere companion of Al but is noticeably enriched. Although it has been shown that complete diadochy exists between Al^{3+} (R_i = 0.57 A) and Ga^{3+} (R_i = 0.62 A), and artificial analogues of feldspars have been prepared [7], it may be supposed that Ga enters more easily into biotite than into feldspar. In the feldspar Al has 4-coordination, but in biotites it occurs also in 6-coordination. For Ga^{3+}, the octahedral coordination insures a stronger Ga-O bond. Because of this, Ga becomes slightly concentrated during the course of crystallization and enriched in the rest magma from which biotite is finally crystallized.

This hypothesis is well illustrated by the nepheline syenite (sp. 268). Here the last minerals to crystallize are biotite and nepheline. Nepheline usually fills spaces between the feldspar crystals. In spite of its late crystallization and high alumina content, nepheline is only half as rich in Ga as the associated biotite. This suggests that the 4-coordination of Al in nepheline served as an obstacle to the entrance of Ga into this mineral and favored its accumulation in biotite, which separated from the melt somewhat later than nepheline. The enrichment of hornblende and augite (sp. 268) in Ga is also apparently due to the later crystallization of these minerals as compared with orthoclase and to the 6-coordination of Al in them.

The low Ga content in augite from sample 265 is evidently due to the high content of this mineral in the sample and to the crystallization of the pyroxene at the time when Ga was dispersed through the rest magma, which still had a rather large volume. The biotite from the same sample has a relatively high Ga content, for it was formed later than augite (the augite is sharply idiomorphic against biotite). Naturally, these considerations are valid only for genetically related minerals formed from the same portion of magmatic melt and are essentially the products of a closed system. The regularities of crystallization of magmas, still little known even for the essential components, are reflected also in the behavior of a trace element. With Ga as an illustration, the authors wish to emphasize the need for considering not only the crystallochemical features of the behavior of trace elements, but also such general features of crystallization as the order of separation of the crystalline phases from the melt and their relative amounts during the process.

The behavior of gallium during the process of differentiation of alkalic magma of the Sandyk Mountains massif.

Table 2 presents the data on the occurrence of Ga in the principal types of alkalic rocks of the Sandyk Mountains massif representing successive differentiates of the same alkalic magma. There is a small but noticeable increase in the concentration of Ga from the earliest to the latest differentiates. Thus, the alkalic gabbroids of phase I contain 18 p.p.m. Ga on the average, while the content of Ga in the nepheline syenites of phase II averages 23-24 p.p.m. As shown in the diagram, this concentration of gallium correlates with increase in the Al content.

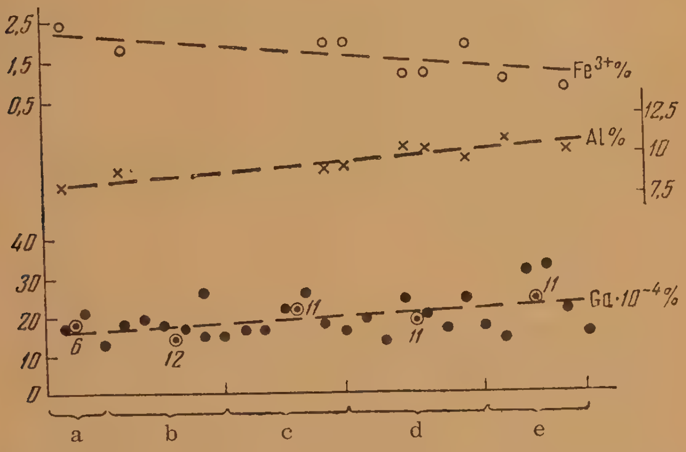
Table 2

Distribution of Ga According to the Rock Type in the Sandyk Mountains Alkalic Massif

Rock type	Areal distribution	Number of samples	Ga content in p.p.m.	
			range of variation	average
Rocks of phase I				
a) Alkalic gabbroids (monzonites -- essexites and monzonite -- shonkinites)	11.4	3	13–21	17
Average rock Ic, mixture of 6 monzonites		6		18
b) Porphyritic calcic syenites, pyroxene -- biotite	35.7	7	15–26	18.4
Average rock IIc, mixture of 12 syenites		12		14
c) Leucocratic calcic syenite facies	31.5	6	16–26	19
Average rock IIIc, mixture of 11 syenites		11		22
Rocks of phase II				
d) Hornblende alkalic syenites	15.0	7	14–24	19.3
Average rock IVc, mixture of 11 syenites		11		19
e) Miaskitic nepheline syenites	6.4	5	16–32	23
Average rock Vc, mixture of 11 syenites		11		24
	100.0 ($\sim$70 km^2)	Average for the massif taking areal distribution of rock types into account		19.3

This fact is confirmed also by the slight deviations of the Ga/Al ratio from the average value of $1.9 \cdot 10^{-4}$, the minimum being $1.2 \cdot 10^{-4}$ and the maximum, $2.3 \cdot 10^{-4}$ (based on 9 analyses). It is interesting to note that the average value lies between the Ga/Al ratios cited by E. B. Sandell [8] for the basic rocks, $1.5 \cdot 10^{-4}$, and granites, $3 \cdot 10^{-4}$.

Thus, in the alkalic rocks of the Sandyk Mountains, gallium accompanied aluminum during the differentiation of magma and was not enriched with respect to it in the course of the process.



Correlation of Ga with Al and Fe^{3+} during the differentiation of alkalic magma of the Sandyk Mountains massif. Early to late rocks are plotted from left to right. The rock types a, b, c, d and e are described in Table 2.

Note. 1) The data for Al and Fe^{3+} are based on chemical analyses of typical samples (L.A. Pevtsova, analyst. Institute of Geochemistry and Analytical Chemistry). 2) Double circle marked by a number indicates analysis of an average sample and gives the number of samples in the mixed sample

According to Higazy [2], in the alkalic volcanic series of southwestern Uganda, Ga content increases with increase in the content of ($Fe_2O_3 + Al_2O_3$) the ugandite-mafurite-katungite series. The diagram given above shows the dependence of the Ga content on the concentration of Fe^{3+} in the alkalic rocks of the Sandyk Mountains. It is clearly seen that in this case the relationship is reversed, i. e., the content of Ga increases as the content of Fe^{3+} diminishes in the course of magmatic evolution. It appears that in the process of differentiation of alkalic magma of the Sandyk Mountains the behavior of Ga was governed by the behavior of Al and not by the behavior of Fe^{3+}, which is crystallochemically akin to Ga^{3+} in its valence and size (Fe^{3+} = 0.67 A).

A comparison of the absolute Ga content in the different alkalic rocks of the Sandyk Mountains massif with its content in other petrochemical types as given in the literature shows few differences. For instance, the authors' figures are near the averages given by Shaw for basic (17 p.p.m. Ga) and intermediate rocks (22 p.p.m. Ga) and are a little higher than Shaw's figures for rhyolites and granites (16 p.p.m. Ga).

The average content for the massif, 19 p.p.m. Ga, is also near Shaw's figure. It is interesting to note, moreover, that the Ga/Al ratio in the Sandyk Mountains massif ($1.9 \cdot 10^{-4}$ on the average) is practically the same as for the diorite magma of the Garabal Hill-Glen Fein complex where this ratio is approximately constant for all rocks and equals $2 \cdot 10^{-4}$ (Nockolds and Mitchell). Exactly the same value of the Ga/Al ratio was obtained for the granitoids of the multiphase Susamyr batholith with an average Ga content of 17 p.p.m. [9].

As compared with some other alkalic rocks, our rocks have a slightly different Ga content. For example, Sandell records 22 p.p.m. Ga_2O_3 (18 · p.p.m. Ga) for a mixture of six syenites from New York and Minnesota. Shaw, in his compilation, mentions that in "true alkalic rocks," the Ga content ranges from 22 to 44 p.p.m. Ga. The Ga content varies within the same limits in some of the alkalic rocks of the Khibina pluton*:

		p.p.m. Ga
1.	Massive khibinite	30
2.	Trachytoid khibinite (with eudialyte)	21
3.	Urtite-ijolite	35
4.	Massive foyaite	18
	Average	26

It will be seen that the figures for the Khibina nepheline syenites are near those for the nepheline syenites of the Sandyk Mountains (24 p.p.m. on the average) in spite of the considerable mineralogical differences between these rocks.

The figures given by Goldschmidt for six samples of nepheline-alkali feldspar rocks of Europe and North America, averaging 50 p.p.m. Ga_2O_3 (or 40.5 p.p.m. Ga), and by Sahama [10] for the syenites of southern Lapland, averaging 74 p.p.m. Ga, must evidently be considered a little high, since these authors used the semiquantitative spectrographic method.

The present investigation shows that the alkalic rocks of the Sandyk Mountains are not particularly enriched in Ga as compared with the other types of igneous rocks. Only the Sandyk nepheline syenites and the closely related nepheline syenites of other regions (for example Khibina) have a slightly higher Ga content.

Table 3 presents data on the occurrence of Ga in some dike rocks of the Sandyk Mountains massif related to both the rocks of phase I and of phase II. In general, the dike rocks are enriched in Ga as compared with the enclosing igneous rocks. The average Ga content in these latest differentiates is 30.6 p.p.m. Ga, and ranges from 13 to 49 p.p.m. Ga. Only in two samples

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*The samples of these rocks were kindly presented by G.N. Ivanova and V.N. Gorstka, to whom the authors express their gratitude.

Table 3

Gallium Content in Some of the Dikes of the Sandyk Mountains Alkalic Massif

Dike rocks	Number of samples	p.p.m. Ga	
		range of variation	average
1. Dike rocks spatially related to phase I (1 leucosyenite, 1 syenite aplite, 2 monzonite porphyries, 1 aplitic syenite)	6	19 – 40	31.0
2. Dike rocks spatially related to phase II (2 leucosyenites, 1 sodalite bostonite, 2 quartz leucosyenites)	5	13 – 49	30.2
Average			30.6

vas the relatively low content of 13 and 19 p.p.m. found. In one of the ikes, syenite aplite with Al content of 8.54% contained 40 p.p.m. Ga and ad the highest Ga/Al ratio, of 4.7 · 10^{-4}. This fact, and also the high Ga ontent in the dike rocks in general, serves to confirm Goldschmidt's opin-on that gallium tends to concentrate in relation to Al in the latest products f magmatic hearths.

It should be noted, however, that, unlike Tl [5], gallium does not re-lect the specific conditions of formation of the dike series in the Sandyk luton. The dike rocks spatially related to the first intrusive phase have he same Ga content as those related to the second phase, although the rincipal rocks of the two phases have slightly different Ga content. Evi-lently it is precisely the absence of any significant difference in the distri-ution of gallium between the two phases that is responsible for this. It nay be suggested, therefore, that the usefulness of Ga in the solution of ome petrological questions will be very limited.

Summary

1. During the process of crystallization and differentiation of alkalic nagma of the Sandyk Mountains massif, the behavior of gallium paralleled hat of Al and was opposite to the behavior of Fe^{3+}.

2. Apart from its close affinity to Al, the distribution of Ga during rystallization of magma depends on the order of separation of minerals nd on the fact that the 6-coordination in the silicates is more favorable or its accumulation than the 4-coordination.

3. The average Ga content for the massif is 19 p.p.m. and the average a/Al ratio, 1.9 · 10^{-4}, with the range of variation between 1.2 p.p.m. nd 2.3 p.p.m. (9 analyses). A slight enrichment in Ga is observed hroughout the development of the intrusive from the initial to the final

stages, and this parallels an increase in the content of Al.

4. The dike rocks genetically related to the pluton of the Sandyk Mountains contain, on the average, 30.6 p.p.m. Ga, i.e., more than the parent rocks.

In conclusion, the authors take the opportunity to thank L. V. Tauson for advice and critical comment during the preparation of the manuscript for the press.

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ON THE URANIUM CONTENT IN PETROLEUM

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(ABSTRACT)

The uranium content is determined in petroleums of some Azerbaijanian deposits bound to different series of tertiary sediments. The uranium determination was carried out in petroleum ash with the aid of the luminescence method.

1. Uranium is a component of all the studied petroleums in which the uranium content varies from 1×10^{-4} to $5 \times 10^{-2}\%$ in the ash or from 1×10^{-7} to 5×10^{-3} g/l of petroleum.

2. The uranium content and the ash content of petroleums are inversely related indicating a bond between the uranium content and the organic petroleum components.

3. The character of uranium distribution in the system petroleum -- sheet waters depends on the chemical composition of the latter. In the above mentioned system the equilibrium is always shifted towards the petroleum but more pronounced in the case of hard waters.

4. It is established that the decrease of the uranium content, being extracted by petroleum from artificial solutions, is in conformity with the following salt series contained in solutions: $CaCl_2$ - $MgCl_2$ - $NaHCO_3$.

Detailed information on the radioactive elements in petroleum and in related organic materials (bitumen, kerogen shales, asphaltites, etc.) is important, not only for the development of organic geochemistry of these elements, particularly uranium, but also for the solution of the complex problem of the origin and migration of petroleum, for the development of the theory and practice of radiometric surveys in the search for oil and gas, and the explanation of the phenomena of concentration of radium isotopes in the oil field waters, of the distribution of radioactivity within oil fields, etc. In spite of this, the content of radioactive elements and especially of uranium in petroleum has been little studied up to date.

The limited data on the uranium content in petroleum available at present are as follows: According to V. A. Unkovskaya's determination [1] the uranium content in five samples of oil from Berekei (Dagestan ASSR), Shubar-Kuduk (Kazakh SSR), and Bibieibat and Naftalan (Azerbaijan SSR) ranges from $2.7 \cdot 10^{-7}$ to $8.2 \cdot 10^{-6}$ g/l in crude oil or from $7.5 \cdot 10^{-5}$ to $3.8 \cdot 10^{-3}$% in the ash.

The presence of uranium in Carpathian oils has been established qualitatively by J. J. Clagoczowski [2]. K. L. Erickson, A. T. Myers and C. A. Horr [3] analyzed 27 samples of oil from different American localities and found from $2 \cdot 10^{-4}$ to $1.4 \cdot 10^{-2}$% of uranium in petroleum ash, or from one to several thousand parts per million in the crude oil.

The present paper reports the results of determinations of uranium in petroleum from a number of Azerbaijan localities. The study covered oils from different stratigraphic units of Tertiary strata (Table 1).

The investigated oils are characterized by an insignificant content of sulfur compounds, absence or very low content of asphaltenes, a small amount of resinous compounds, and high content of naphthenic acids [4]. Among the petroleums analyzed for uranium there are oils with a strong naphthene base (from the upper zones of the Surakhan field). The content of the light fractions distilled at temperatures up to 300°C ranges from 25 to 77%. The specific gravity varies rather widely, from 0.760 to 0.920. The specific gravity and the content of resinous compounds increase with depth of the pool, while the light fraction decreases. The ratio of the resinous compounds to the asphaltenes in all investigated petroleums is greater than unity, indicating that they had not undergone weathering.

The samples of petroleum were collected directly from producing wells, several samples from each at different times. The oil was carefully separated from mechanical admixtures and water, including emulsion water, by prolonged standing, filtration, and heating on a water bath with a return condenser at 70°C.

The petroleum samples, purified from mechanical admixtures and water, were evaporated in porcelain cups until coke was formed. The coke was reduced to ash in a muffle furnace at 450-500°C. The ash was treated with a mixture of nitric and hydrochloric acids and boiled. Uranium was extracted from the solution with charcoal by the method developed by P. N. Zharov. Uranium was determined by luminescence.

The data on the uranium content in the petroleums, given in the Table, show that uranium is present in the ash of all investigated petroleums. Its content varies within broad limits, from 1.10^{-4} to $5 \cdot 10^{-2}$% in the ash and from $1 \cdot 10^{-7}$ to $5 \cdot 10^{-5}$% in the crude oil. The ratio of the extreme figures is 500. With rare exceptions, the essentially naphthene petroleums from the Balakhan and Surakhan formations have the highest uranium content. As the table shows, the petroleums from these formations in all fields contain ten and even a hundred times as much uranium as the oils from other formations. The data on the Surakhan and Bibieibat localities shows this especially well.

There is, moreover, a clear relation between the uranium and ash content in the petroleums, for as the latter increases, the uranium content diminishes. This relation is shown by the correlation coefficient: $\underline{r} = -0.46$* and the graph (Fig. 1).

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* The data of 56 analyses were used in computing the correlation coefficient.

Deposit	Formation	Horizon	Ash, %	Uranium content	
				in ash, 10^{-4}%	in oil, 10^{-6}%
Balakhany	Apsheron	Apsheron, stage 1	0,0481	4,2	2,0
»	Sabunchi	IV	0,0192	3,1	0,6
»	Balakhany	VI	0,0085	12,9	1,1
»	»	VIII	0,0157	3,8	0,6
»	»	X	0,0100	2,0	0,2
»	Nadkirmakinskaya	NKP_1	0,0390	6,4	2,5
»	Kirmakinskaya	IKC_1	0,0208	1,0	0,2
	»	PKC_1	0,0300	5,0	1,5
	Podkirmakinskaya	PK_1	0,0250	6,0	1,5
Surakhany	Surakhany	SD	0,0032	18,7	0.6
	Sabunchi	II - Pa	0,0012	500,0	6,0
»	»	III	0,0050	8,8	0,44
»	»	IV	0,0086	70,0	6,0
»	Balakhany	VI	0,0110	182,0	20,0
»	»	VII	0.0100	500,0	50,0
»	Nadkirmakinskaya	NKG	0,0090	2,2	0,2
»	»	NKP	0,0078	9,6	0,75
»	Kirmakinskaya	III - KS	0,0100	200,0	20,0
»	Podkirmakinskaya	PK_2	0,0430	1,0	0,43
»	»	PK_4	0,0500	1,2	0,6
Bibieibat	Sabunchi	P - IIIp	0,0520	96,0	50,0
»	»	IV—V	0,0107	20,0	2,0
»	Balakhany	V	0,0190	53 0	10,0
»	»	VII	0,0700	2,8	2,0
»	»	X	0,0210	200,0	41,6
»	»	XIII	0.0170	2,7	4,6
»	Nadkirmakinskaya	NKG_1	0,0440	9,5	4,2
»	»	NKP_1	0,0440	45,0	20.0
»	Kirmakinskaya	1 KS	0,0480	4,1	2,0
»	»	III KS	0.0116	3,4	0,4
»	»	VKS	0,0240	25,0	5,8
»	Podkirmakinskaya	PK_1	0,0480	87,0	42,0
Binagady	»	KS_2	0,0150	5,2	1,0
»	»	KS_4	0.0750	2,7	2,0
»	»	KS_5	0,0140	2,9	0,4
Umbaki	Maikop	III	0,0760	3,2	2,4
»	»	III	0,0135	11,8	1,6
»	»	III	0,0203	2,0	0,4
»	»	III	0,0205	3,0	0,6
»	»	IV	0,0225	3,0	0,6
Astrakhanka	Cretaceous		0,0079	7,6	0,6
	»		0,0690	1,1	0,8
	»		0,0280	3,2	0,9

Note: Comma represents decimal point.

It is pointed out in the literature that the heavy metals in the petroleum sh are present in the mechanical admixtures and that their content is acidental [15]. The inverse relationship between the uranium and ash connt in the oils indicates that uranium cannot be associated in them with the ccidental mechanical admixtures but is present in the organic components f petroleum.

Petroleum is constantly in more or less mobile contact with the reseroir rocks and waters. Academician V. I. Vernadskii once expressed the

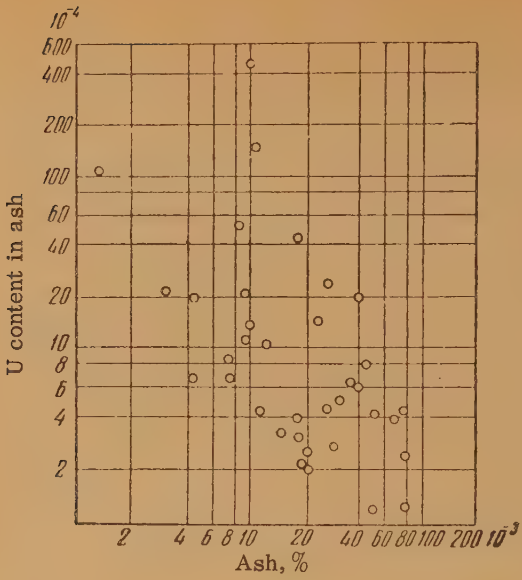

Fig. 1. Dependence of uranium content in petroleum ash on the ash content in petroleum

idea that "... radium (and possibly uranium) is in mobile equilibrium between the petroleum and the water of the reservoir rock" [6].

In order to characterize this equilibrium to some extent, uranium was determined in the waters associated with petroleum. The waters, as is known [7], are of two hydrochemical types: 1) the hard, sodium-calcium chloride waters of high salinity in the upper part of the productive beds and of the Aspheron formation and 2) the alkaline sodium carbonate waters of relatively low salinity occurring in the lower part of the productive strata of the Maikop and other formations. A comparison of the results of the determination of uranium in the petroleums and in the associated waters shows that there is no strict relationship between the uranium content in the oils and in the waters. However, the (uranium in petroleum) - (uranium in water) ratios given in Fig. 2 indicate that the equilibrium is strongly shifted towards petroleum. Moreover, there are two clearly distinguishable cases: 1) the petroleum-hard water system and 2) the petroleum - alkaline water system. In the first of these, the shift of equilibrium in the distribution of uranium towards petroleum is more pronounced and is related to the salt composition of the water.

This relationship was checked by special experiments on the extraction of uranium by petroleum from prepared solutions of salts found in the reservoir rock waters. To the solutions of $NaHCO_3$, $NaCl$, $MgCl_2$ and $CaCl_2$, $1 \cdot 10^{-4}$ moles of uranyl nitrate were added and the solutions were brought in contact with petroleum under dynamic conditions. Equilibrium in the distribution of uranium was attained in the first two hours. After separation

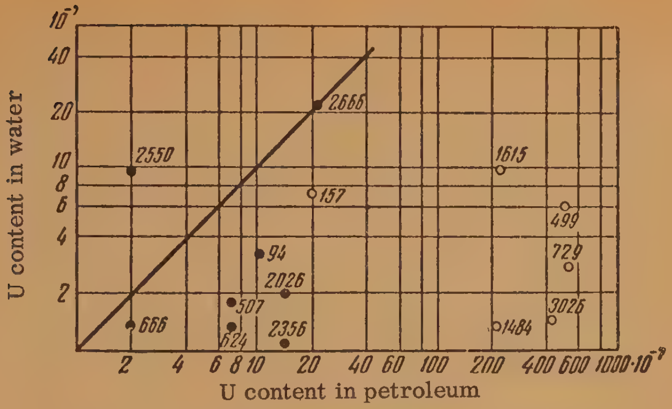

Fig. 2. Uranium content in petroleum and in associated waters

● -- alkaline waters
o -- hard waters

of petroleum and the solution, the amount of extracted uranium was determined. The results, shown in Fig. 3, indicate that the amount of uranium extracted by petroleum from the different salt solutions decreases in the following sequence:

$$CaCl_2 \text{ -- } MgCl_2 \text{ -- } NaCl \text{ -- } NaHCO_3.$$

This dependence of the partition of uranium between petroleum and the solutions on the composition of the latter is evidently one of the causes of

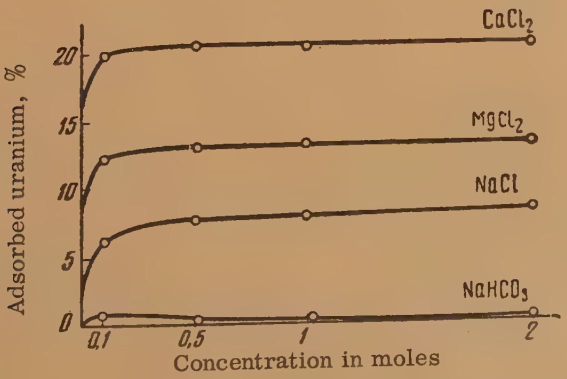

Fig. 3. Extraction of uranium by petroleum from salt solutions of different concentrations

the stronger enrichment in uranium of the sodium carbonate waters as compared with the calcium chloride waters. This fact was established by A. N. Nuriev and G. Kh. Efendiev [8] and also by F. A. Alekseev, V. I. Ermakov and V. A. Filonov [9].

Thus, there is a definite connection between the content of uranium in petroleum and the hydrochemical type of the associated waters.

The source of uranium in petroleum may be considered on the basis of this dependence. Two modes of accumulation of uranium in petroleum are possible.

1. Uranium may be inherited by petroleum from the mother-substance. In the course of geologic time, during migration and accumulation in the reservoir rocks, as a result of constant contact with deep-seated waters and repeated attainment and destruction of equilibrium, uranium may be repeatedly distributed and redistributed between petroleum and water.

This process must result in impoverishment of petroleum in uranium. Depending on the type of water in contact with petroleum, the latter will be impoverished in uranium to a greater or less degree. For example, on the Apsheron Peninsula the petroleums of the upper part of the productive strata associated with hard waters must contain more uranium than the petroleums of the lower part, where alkaline waters are predominant. This is actually the case.

2. The petroleum may accumulate uranium during migration by extracting it from the waters. The sources of uranium are the sedimentary rocks containing both petroleum and water. According to the analyses of the claystones and sandstones predominating in the petroliferous strata of Apsheron Peninsula, their uranium content is the average for sedimentary rocks, i. e., $4.1 \cdot 10^{-4}$ and $2.55 \cdot 10^{-4}\%$, respectively.

It is interesting to note that the figure cited for the claystones agrees entirely with the data of V. I. Baranov, A. B. Ronov and K. G. Kunasheva [1] on the claystones of the Russian platform.

It is difficult to determine which of these two sources was the more important in contributing uranium to petroleum. It is clear, nevertheless, that the joint migration of petroleum and water and the chemical type of the water associated with the petroleum had a strong influence on the quantitative distribution of uranium in petroleums from the upper and lower parts of the productive strata.

Summary

1. In the 56 petroleum samples systematically collected from the main petroliferous formations and zones in the Azerbaijan oil fields, uranium is present in amounts ranging from $1 \cdot 10^{-4}\%$ to $5 \cdot 10^{-2}\%$ in the ash and from $1 \cdot 10^{-7}$ to $5 \cdot 10^{-5}$ g/l in the crude oil.

2. The content of uranium is in reciprocal relation to the ash content in the petroleum, suggesting that it is related to its organic components.

3. The character of distribution of uranium in the petroleum - water system depends on the chemical composition of the water. The equilibrium in this system is always shifted towards petroleum but more so in the case of water of high salinity.

4. Experiments show that the amount of uranium extracted by petroleum from prepared solutions of different salts diminishes in the following sequence: $CaCl_2$ -- $MgCl_2$ -- $NaCl$ -- $NaHCO_3$.

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THE DISTRIBUTION OF RHENIUM IN MOLYBDENITES FROM DEPOSITS OF A SERIES OF GENETIC TYPES

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(ABSTRACT)

The rhenium content is determined in 19 molybdenites from deposits of two genetic types of the Central Kazakhstan.

The average rhenium content in molybdenites from high temperature rare metal deposits (Kara-Oba, Akchatau, Airshoko, Dal'nenskoe) is 2.5 p.p.m. at a fluctuation from 1 p.p.m. to 5.6 p.p.m. In deposits of the middle-temperature type (Shalgia) the average content is considerably higher and amounts to 32 p.p.m. at a fluctuation of 22 to 39 p.p.m.

A comparison with the data obtained with the results of molybdenite analyses from deposits of other types (skarn and copper - molybdenite types) shows the existence of a general regularity in the increase of rhenium content in molybdenites with a fall of the temperature of deposit formation.

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1. The entry of rhenium into molybdenites is an example of endocryptism, explained by the closeness of the chemical and crystallochemical properties of rhenium and molybdenum. Nevertheless, up to the present, many features of the geochemistry of rhenium are still not apparent or remain unclear. Thus, in the clearly expressed chalcophilic properties of rhenium, it is unexpected that it is accumulated in certain rare earth minerals of Norwegian and other pegmatites; besides, it accompanies in generally rather large amounts of sulfide-forming heavy metals, not forming a close assocation with anyone of these. This may be explained by the fact that in these minerals rhenium enters in the sulfide form, which is confirmed by the studies of W. and I. Noddack [1]. In other minerals - albite, columbite, and tantalite - the amount of sulfidic sulfur is so small that rhenium probably, in the opinion of the Noddacks, enters them in the oxide

form. Thus, rhenium, in one and the same group of rare-earth pegmatite minerals, might enter them in different forms, which seems unlikely.

It is probable, all told, that the appearance of rhenium in rare-earth minerals is associated with the late hydrothermal processes of pegmatites, which might be either simultaneous with the pegmatite formation or superimposed after some interval of time [2]. Associated with these processes may be the appearance of a whole series of elements, particularly in rare-earth minerals.

One might assume that because of the closeness in properties of rhenium and molybdenum, the ratio of the amounts of these elements might appear as a characteristic magnitude or an independent geochemical indicator of some processes. For molybdenites containing the maximum amounts of rhenium, the ratio Mo:Re is n x 10^3, where n is close to, and in some cases less than one. According to the data of the Noddacks, approximately this ratio (10^3) is characteristic for most hypogene sulfides, increasing (up to n x 10^4) for sulfides of sedimentary genesis. For rare-earth pegmatites of pegmatites the ratio decreases sharply to 10^2. It is possible that this is explained by the following facts. First, the low ratio Mo/Re may be generally characteristic of pegmatitic process. But this is contradicted by the data of S. M. Basitova [3, see further]. Or, this ratio may be characteristic only for pegmatites of a specific type or for specific regions. Second, this ratio may reflect the conditions at the time of precipitation of molybdenum and rhenium in the rare-earth minerals during their hydrothermal alteration. Third, it is possible that one must take into account the effects of processes of oxidation, which can cause the predominant migration of rhenium, whereby there occurs its secondary relative enrichment in some minerals as a consequence of sorption.

The content of rhenium, i. e. the ratio Mo/Re, in molybdenites varies over a wide range. It is known that some molybdenites are greatly enriched in rhenium – they contain up to n x 10^{-2}%; at the same time molybdenites or rare metal deposits sometimes contain in all up to 5 x 10^{-6}% rhenium (= 0.05 p.p.m. Re). According to the Noddacks [1], the ratio Mo/Re in molybdenites from veins at Telemark, Norway, varied regularly from one side to the other from 10^{-6} to 10^{-5} p.p.m. On the basis of the analysis of a series of samples, S. M. Basitova [3] drew the conclusion that the rhenium content of molybdenites increased with the transition from high-temperature deposits to medium-temperature deposits. From consideration of the data of Z. V. Studenikova and V. A. Zolotareva [4], one may draw the conclusion that for the Tyrny-Auz deposits studied by these authors no specific conclusions can be drawn as yet as to regularities in the distribution of rhenium in the molybdenites. The content of rhenium in the molybdenites of these deposits varied in the limits of two orders of magnitude, in all not exceeding n x 10^{-4}%.

2. With the aim of obtaining supplementary data on the problems of interest to us, we analyzed pure molybdenites from four high-temperature rare-metal deposits of Central Kazakhstan: Kara-Oba, Akchatau, Airshoko, and Dal'nensk, and also from the Shalgiya deposit, belonging to the lower-temperature molybdenite-pyrite type.

The first four deposits are spatially and genetically related to intrusives of leucocratic granites, which are considered to be typical representatives of the late Hercynian cycle. Determinations of the age give for the Akchatau deposits about 300 million years.

Molybdenum deposits of the given type are usually veins, rarely stockworks associated with numerous quartz veins of different widths. The mineralogical composition of the veins is rather complex. Their main ore minerals are wolframite, molybdenite, and cassiterite; of the sulfides; pyrite and others; gangue quartz, feldspar, micas, fluorite, rarely topaz, beryl, and others. Intense alteration of the country rock - their greisenization - is characteristic near the veins.

In the Kara-Oba deposit, studied in more detail, there were separated several types of quartz veins. To the high-temperature type were referred quartz-molybdenite with feldspar, quartz-cassiterite, and quartz-wolframite veins, from a combination of indications such as the structural relations (crossing veins), mineralogical composition, and near-vein alteration (absence of greisen alteration near the quartz-molybdenite veins). The quartz-molybdenite veins are considered the earliest, the quartz-wolframite the latest. The position of the quartz-cassiterite veins is not entirely clear; apparently they are intermediate in time of formation between the two types mentioned. The quartz-molybdenite type of vein is characteristic of the southwestern (molybdenum) part of the deposit, where it forms stockworks of quartz-molybdenite veinlets and a series of wide down-dipping veins of the same composition, occurring in enclosing intrusions of effusives. In the central part of the deposit, associated with granites, with a predominant development of quartz-wolframite veins, there are known several quartz-molybdenite veins, analogous to the veins of the southwestern part. In the quartz-molybdenite and quartz-wolframite veins, molybdenite forms coarse rosettes or fine-platy accumulations. In the quartz-cassiterite , the medium-temperature quartz-wolframite with sulfides of Fe, Zn, and Pb, and low-temperature veins, molybdenite is not found. For analysis there were selected samples of monomineralic molybdenite from the quartz-molybdenite and quartz-wolframite veins of the central and southwestern parts.

The Shalgiya deposits are stockworks, consisting of veins and veinlets of quartz-molybdenite with disseminations of pyrite associated with altered granite. Characteristic features of the deposit are the fine dispersed occurrence of molybdenite in the ore-bearing quartz, thanks to which it has a bluish-gray color. The mineralogical composition of the veinlets is simple: quartz predominates, with small amounts of sericite, molybdenite, and pyrite. In the formation of the deposit a large role was played by metasomatic processes, expressed in the strong sericitization and silicification of the enclosing granite. The absence of high-temperature minerals and the type of near-vein alteration show the relatively lower-temperature character of the ore-forming solutions. For analysis there were separated samples of monomineralic molybdenite from the ore-bearing quartz with fine-dispersed molybdenite and the later monomineralic molybdenite veinlets, associated with zones of tectonic disturbances.

Besides the samples enumerated, there were also taken individual samples of molybdenite from the Akchatau, Airshoko, and Dal'nensk deposits. For all the samples the determination of rhenium was carried out by the colorimetric method, based on the ability of rhenium to give a colored thiocyanate complex in a two normal HCl solution medium in the presence of stannous chloride as reductant [5]. The accuracy of the method for determining the rhenium contents is +10%; the sensitivity is about 0.18 gamma/mg.

The analyses are given in Table 1.

Table 1

Rhenium in molybdenites of deposits of Central Kazakhstan

No.	Deposit	Place of Collection of monomineralic sample	Content Re p.p.m.
		Southwestern Part	
1	Kara-Oba	Quartz-molybdenite dipping vein 54 with feldspar	2.0
2		Quartz-molybdenite " " "	3.7
3		" " " " "	2.9
4		Quartz-molybdenite veinlet stockwork, steeply dipping, in effusives	2.3
5		Quartz-molybdenite veinlet stockwork, dipping, in effusives	3.0
6		Quartz-molybdenite veinlet stockwork, dipping, in granite	1.0
		Central Part	
7		Quartz-molybdenite dipping vein	4.3
8		" " " "	5.0
9		" " steeply-dipping vein	5.8
10		" " " " "	5.2
11		Quartz-wolframite veins 10 and 1	1.0
12		" " vein 2-v	1.4
13	Akchatau	Quartz veins with coarse platy molybdenite and pyrite (southwest part)	1.2
14	Airshoko	Quartz veins with molybdenite and muscovite	2.7
15	Dal'nensk	Quartz veins with coarse platy molybdenite	2.2
16	Shalgiya	Metasomatic quartz with fine-dispersed molybdenite	32
17		Metasomatic quartz with fine-dispersed molybdenite	34
18		Metasomatic quartz with fine-dispersed molybdenite	39
19		Monomineralic molybdenite veinlets in quartz	22

DISCUSSION OF THE RESULTS

The average content of rhenium in molybdenites of the Kara-Oba deposits is ~ 3.3 p.p.m. Analyses of samples of quartz-molybdenite veins of the southwestern part showed that their content of rhenium ranged from 1.0 to 3.7 p.p.m. and averaged about 2.5 p.p.m. Samples from the quartz-molybdenite veins of the central part contain 4.3 to 5.8 p.p.m. Re, average

5.0 p.p.m., i.e. more than the analogous veins of the southwestern part. The lowest contents of rhenium were found in the molybdenites of the quartz-wolframite veins, averaging about 1.2 p.p.m.

Thus, on the basis of the rhenium content, one may separate three groups of molybdenites: 1) from the quartz-molybdenite veins of the central part, characterized by the highest content of rhenium - 5.0 p.p.m; 2) from analogous veins of the southwestern part, containing less rhenium - 2.5 p.p.m.; and 3) from the quartz-wolframite veins, characterized by the lowest content of rhenium - 1.2 p.p.m.

It is seen from Table 1 that the content of rhenium in the molybdenites of the Akchatau, Airshoko, and Dal'nensk deposits are in general of the same order of magnitude as for the Kara-Oba deposit. The small number of analyses available does not permit us to discuss in more detail the features of the behavior of rhenium for these deposits.

For the average content of rhenium in molybdenites of deposits of this type, one may assume a magnitude of about 2.5 p.p.m.; the range of content is 1.0 to 5.6 p.p.m., i.e. about 5-1/2 fold. If one compares these data with those for the content of rhenium for the Tyrny-Auz deposits, for which [4] the average is 3.2 p.p.m. with a range of 0.1 to 14 p.p.m., one may draw the conclusion that the order of magnitude of the rhenium contents in these deposits are the same, whereas the variation of the content are much greater.

For the Shalgiya deposits, four samples were analyzed. Their average is 32 p.p.m. with a variation of 22 to 34, i.e. their content of rhenium is an order of magnitude higher than that of the molybdenites of Kara-Oba.

The samples of molybdenites analyzed from these two deposits were also analyzed by semi-quantitative spectrographic analyses. They showed that for all the molybdenites the presence of one and the same elements is characteristic - Pb, Bi, Cu, Ag, in similar concentrations.

According to the available data, there has been established in the molybdenites of the copper-molybdenum deposits of Kajaran (Armenia) 160-320 p.p.m. Re and in enriched veinlet-disseminations of molybdenum ores 270-410 p.p.m. Re, in molybdenites of the Aigedzor deposit 780 p.p.m., of Kounrad 150 p.p.m. Consequently, the content of rhenium is not less than 100 p.p.m. in molybdenite deposits of this type, i.e. the highest of the known concentrations of rhenium.

In Table 2 are given the average contents of rhenium obtained for the Kara-Oba and Shalgiya deposits, the determinations for individual samples of the Akchatau, Airshoko, and Dal'nensk deposits, and also some data from the literature.

If one compares the contents of rhenium in the molybdenites of different deposits, given in Table 2, one may draw the conclusion: the concentration of rhenium in molybdenites in general changes sharply with the transition from the genetic high-temperature type (adopted universally recently as a classification means) towards the lower-temperature types; with the boundaries of a single genetic type, the deviation is small. The concentration of rhenium in the molybdenites increases with transition towards the low-temperature type of deposit.

W. and I. Noddack [1] based the geochemistry of rhenium in the post-magmatic stages on differences in the volatility of the chlorides of rhenium and molybdenum, and also on the high solubility of perrhenates. In their opinion, in the process of cooling the magma, molybdenum to a greater than rhenium is likely to enter into crystallizing minerals. The residual melt is thereby gradually relatively enriched in rhenium. The subsequent

Table 2

Contents of rhenium in molybdenites of deposits of various genetic types

Genetic type of deposit	Name of deposit	Average content of Re, p.p.m.	Reference
Skarn	Tyrny-Auz, Northern Caucasus	$3.2 \cdot 10^{-4}$	[3]
Cassiterite-wolframite-molybdenite (high-temp.)	Kara-Oba	$3.3 \cdot 10^{-4}$	This paper
	Akchatau	$1.2 \cdot 10^{-4}$	
	Airshoko	$2.7 \cdot 10^{-4}$	
	Dal'nensk, all Central Kazakhstan	$2.2 \cdot 10^{-4}$	
Molybdenite-pyrite (transitional from the high-temperature toward the medium-temperature)	Shalgiya, Central Kazakhstan	$3.2 \cdot 10^{-3}$	This paper
Molybdenite-chalcopyrite (copper-molybdenum, medium-temperature)	Kounrad, Central Kazakhstan	$1.5 \cdot 10^{-2}$	[3]
	Kajiran, Armenia	$1.6\text{-}4.1 \cdot 10^{-2}$	
	Aigedzor,	$7.8 \cdot 10^{-2}$	

reaction of halides with the residual magma extracts rhenium and molybdenum, and the later that this takes place, the higher will be the contents of rhenium in the molybdenites of pneumatolytic genesis. In the presence of liquid water at temperatures below 350°, the anion ReO_4 is formed, and rhenium is dispersed in sulfides in so large a degree as the amount and length of time that water took part in their formation.

At present it is uncertain whether it is possible to give an acceptable explanation of the features of the behavior of rhenium in the post-magmatic stages, because as yet there are too few factors characterizing the features of its geochemistry, and experimental work is lacking on the study of its behavior at high temperatures and pressures. The ideas of the Noddacks on the form of transport of rhenium, especially on its entry into hydrothermal solutions in the form of per-rhenates, can not be accepted and provoke doubt without experimental verification.

The problem of the reason for the differences in concentration of rhenium in molybdenites or the different ratios Mo/Re in other minerals of deposits of different genetic types is rather complex. One may assume that one of the main factors in the given cases will be the temperature of formation of the molybdenites or molybdenum-containing minerals. It is possible also that of decisive significance are:

(1) the content of rhenium (ratio Mo/Re) in the original oreforming solution, which generally also ought to depend on the content of rhenium in the original magma; (2) the pressure and the character of the volatiles, among which is the concentration of sulfur at the time of crystallization of the molybdenite.

The variation in the content of rhenium in molybdenites from one and the same deposit, but taken from different parts of it, or even in one and the same vein, may possibly be connected with the different ratios of molybdenum and rhenium in different parts of the ore solutions and the more local and fine physical-chemical features of the formation of molybdenite. One must bear in mind that the intrinsic magnitudes may have regional features, i. e. deposits of a specific region may be distinguished by generally higher or lower contents of rhenium in molybdenites.

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CONCLUSIONS

1. The content of rhenium in molybdenites of the high-temperature rare-metal deposits of Central Kazakhstan range from 1 to 5.6 p.p.m., averaging 2-3 p.p.m. For the Kara-Oba deposit the average content of rhenium is 3.3 p.p.m.
2. For the medium-temperature deposit of Shalgiya, referred to the molybdenite-pyrite type, the content of rhenium ranges from 22 to 39 p.p.m., averaging 32 p.p.m.
3. The content of rhenium in the molybdenites of deposits of various types increases from the skarn and high-temperature types (averaging $n \times 10^{-4}\%$ Re) to the transitional medium-temperature molybdenite-pyrite type (averaging $n \times 10^{-3}\%$ Re) and further to the relatively low-temperature copper-molybdenum type (averaging $n \times 10^{-2}\%$ Re).

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DISTRIBUTION OF RUBIDIUM AND THE K/Rb RATIO IN THE ROCKS OF THE LOVOZERO ALKALIC MASSIF

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(ABSTRACT)

The average rubidium content in nepheline syenites of the Lovozero alkaline massif is 210 g/t of Rb and the K/Rb ratio is 195.

An increase of the rubidium contents and a corresponding decrease of the K/Rb ratio in rocks of younger intrusive phases compared to more ancient phases is noted.

It is known that in the course of magmatic evolution potassium and rubidium accumulate in the younger intrusive rocks.

The regular decrease in the K/Rb ratio during the course of emplacement of multiphase intrusions has been demonstrated by Nockolds and Mitchell [8], A. M. Dёmin and D. N. Khitarov [4], and other investigators. Thus, the K/Rb ratio may serve as a geochemical index of the age sequence of intrusive phases in magmatic complexes.

The complexly differentiated Lovozero alkalic intrusion (Kola Peninsula) provides an excellent opportunity for the use of the K/Rb ratio in determining the sequence of formation of alkalic rocks.

The distribution of rubidium in nepheline syenite massifs is little known [9]. The recently published paper by V. I. Gerasimovskii and V. I. Lebedev [3] contains only preliminary information, requiring amplification and refinement.

The structure of the Lovozero massif, according to Gerasimovskii's data, is as follows:

The alkalic intrusion cuts through the Archean metamorphic rocks and contains xenoliths derived from the Upper Devonian sedimentary-effusive beds of the roof.

The alkalic rocks of the massif form four complexes corresponding to four intrusive phases:

Phase I includes poikilitic, porphyritic and equigranular nepheline syenites, and hydrosodalite syenites. It is represented by occasional xenoliths in the rocks of the later phases.

Phase II consists of lujavrites, foyaites, and urtites forming a complexly differentiated rock complex over 1400 m in thickness. The alternation of the bodies of lujavrites, foyaites, urtites, and associated rocks gives this complex a stratified aspect.

Phase III consists of eudialyte lujavrites and associated porphyritic lujavrites. It is represented by an intrusive body up to 450 m in thickness, which cuts the rocks of the second intrusive phase and forms the upper part of the massif. Small bodies of poikilitic sodalite syenites and tawites are associated with the third intrusive phase (III A phase).

Phase IV includes a few thin dikes of alkalic gabbroids of the biotite monchiquite type and other rocks.

The samples of the most typical nepheline syenites of the massif were selected for rubidium determinations.

According to M. D. Dorfman [5], nepheline is intensively decomposed by supergene processes and the alkalies are removed from it, first of all, while the feldspars are relatively stable under the conditions of weathering. To check this, both unaltered and zeolitized samples of nepheline syenites of the Lovozero massif were analyzed for rubidium.

The obtained data (Table 1) indicate that the zeolitized urtites have lost over 50% of rubidium as compared with the unaltered rocks and are therefore useless for analysis. The rubidium content in the other types of nepheline syenites and especially in melanocratic rocks is substantially changed, not by zeolitization.

Table 1

Rubidium Content in Unaltered and Zeolitized Nepheline Syenites, p.p.m.

Rock	Melanocratic lujavrite	Foyaite	Urtite
Zeolitized nepheline syenites	165	200	110
Unaltered nepheline syenites	150	265	230

Rubidium was determined spectrographically. The light souce was a self-igniting a-c arc operated at 220 volts and 7 amp. Exposure time was 5 minutes.

To equalize the composition of the samples, 50% KCl was added to each one. The samples mixed with KCl were placed in the cavity of the electrode 4.5 mm deep. The samples weighed 40 mg.

The spectra were photographed on a glass spectrograph ISP-51 with a camera of 270 mm focal length on infrachrome-840 plates. The 0.05 mm wide slit was illuminated with a two-lens system. A two-step weakener was used in front of the slit.

The two most intensive rubidium lines, 7800.23 and 7947.60A, were used in the analyses.

The calibration curves were constructed on the coordinates S and log C, where ΔS is the difference between the density of the line and the adjacent background. The relative error of the method as determined by repeated measurements was ± 9%.

The standards were rock samples in which rubidium content had been carefully determined in solution by flame photometry and spectrographically with a self-igniting a-c arc as the source of light. The samples were introduced into the arc by means of a fulgurator.

The results of analyses of the nepheline syenites for rubidium are presented in Table 2.

The distribution of rubidium in the first intrusive phase is uniform. It is interesting to note that the rocks in which nepheline syenite has been replaced by hydrosodalite, the so-called hydrosodalite syenites, have the same rubidium content as the common nepheline syenites.

The average rubidium content calculated for some xenoliths in the rocks of the first phase shows a slight variation from 120 g/ton Rb in the region of Mt. Ninchurt to 160 g/ton in the region of Mt. Punkaruaiv. The average rubidium content in nepheline syenites of phase I is 140 g/ton Rb (average of 14 analyses).

Among the nepheline syenites of the second phase the foyaites are the richest in rubidium (average of 5 analyses -- 245 g/t Rb), the urtites and malignites contain 165 g/t Rb (average of 7 analyses), and lujavrites 190 g/t Rb (average of 10 analyses). Table 2 shows that the feldspathic nepheline syenites (foyaites) are much richer in rubidium than the urtites in which nepheline is the dominant component. It should be noted that the melanocratic rocks (amphibole lujavrites, melanocratic lujavrites, and loparite-bearing lujavrites) contain less rubidium than the leucocratic (foyaites and urtites).

According to the latest data of A. I. Polyakov and Yu. A. Balashov (oral communication), the average thickness of the lujavrite-foyaite-urtite complex is 1400 m, the lujavrites accounting for 60%, the foyaites for 35.5% and the urtites for 4.5% (volume percent). Accordingly, the average Rb content in the rocks of the second intrusive phase is 205 g/t. This is a tentative figure, for the lower horizons of the complex recently reached by drilling have not yet been analyzed for rubidium.

The distribution of rubidium in eudialyte lujavrites and associated porphyritic lujavrites (phase III) is rather irregular. The average rubidium content in eudialyte lujavrites is 230 g/ton Rb (average of 7 analyses), and in porphyritic lujavrites 250 g/ton Rb (average of 6 analyses). According to N. A. Eliseev [7], the average content of potassium in the eudialytites is 1.21% and their rubidium content is correspondingly low as compared with other rocks of phase III (85 g/ton).

Like the urtites of the second phase, the porphyritic juvites, containing 70% nepheline, have a low rubidium content (150 g/ton Rb). The eudialyte lujavrites constitute 95% of the volume of rocks of the third phase and the porphyritic lujavrites 5%. Hence, the average Rb content in the rocks of the third phase is 230 g/ton (not counting eudialytites and porphyritic juvites occurring in occasional small bodies). The poikilitic sodalite syenites

Table 2

Rubidium Content in the Rocks of the Lovozero Massif

Sample number	Locality	Rock	Rb p.p.m.
First intrusive phase			
139	Mt. Ninchurt	Coarse-grained nepheline syenite	110
69	"	Coarse-grained nepheline syenite	100
68	Mt. Alluaiv, hole 167	Porphyritic nepheline syenite	140
183	"	Medium-grained nepheline syenite	150
185A	"	Coarse-grained nepheline syenite	150
188B	"	Medium-grained nepheline syenite	140
193	" hole 187	Fine-grained nepheline syenite	165
196	"	Poikilitic hydrosodalite syenite	150
66	Mt. Suoluaiv	Poikilitic nepheline syenite	150
66A	"	Fine-grained nepheline syenite	150
72	Mt. Punkaruaiv	Poikilitic nepheline syenite	150
75	"	Poikilitic nepheline syenite	130
77	"	Coarse-grained nepheline syenite with hydrosodalite	185
431	Tavaiok River	Poikilitic hydrosodalite syenite	140
Second intrusive phase			
190	Mt. Alluaiv, hole 167	Lujavrite with loparite	165
264	Shomiiok River	" "	155
8	Mt. Karnasurt, hole 107	Amphibole lujavrite	150
19	"	" "	160
23	Mt. Karnasurt, hole 100	Mesocratic lujavrite	190
26	"	" "	260
26B	" hole 100	Leucocratic lujavrite	250
28	"	Melanocratic lujavrite	210
34	Mt. Alluaiv, hole 187	" "	175
362	Mt. Parguaiv	" "	165
182B	Mt. Alluaiv, hole 167	Foyaite	290
272	"	"	240

Table 2 (Continued)

Sample number	Locality	Rock	Rb p.p.m.
143	Mt. Karnasurt, hole 82	Foyaite	210
144	" hole 107	"	265
38	Mt. Alluaiv, hole 187	"	210
187	" hole 167	Urtite	230
276	"	Urtite with loparite	230
363	Mt. Parguaiv	"	140
14B	Mt. Karnasurt, hole 107	Ijolite-urtite	195
268	Shomiiok River	Urtite with apatite	140
XIX	Mt. Kuftn'yun	" "	140
1367	Mt. Karnasurt	Malignite with loparite	110
	Third intrusive phase		
160	Mt. Alluaiv	Eudialyte lujavrite	165
245	"	" "	290
168a	" hole 167	" "	200
168b	"	" "	195
165	"	" "	210
49	Mt. Karnasurt, hole 83	" "	300
50a	"	" "	240
XXI	Mt. Flora	Porphyritic lujavrite with murmanite	200
249	Mt. Alluaiv, hole 167	Porphyritic lujavrite with murmanite	240
170	"	Porphyritic lujavrite	300
263	Elemaraiok River	Porphyritic lujavrite with lovozerite	290
106	Mt. Vavnbed	Porphyritic lujavrite with lovozerite	340
246	Mt. Alluaiv	Porphyritic Juvite with loparite	150
110	Mt. Vavnbed	Eudialytite	85
104	"	Pokilitic sodalite syenite	175
266	Tyul'bn'yunuai River	" " "	130
141	Chinglusuai River	" " "	165
92	Uel'kuai River	" " "	150
430	Tavaiok River	Tawite	110
	Fourth intrusive phase		
XXII	Mt. Alluaiv, hole 165	Monchiquite	80
1393	Mt. Karnasurt, hole 83	Monchiquite	80

and tawites (phase III A) are genetically related to the eudialyte lujavrites. They contain 150 g/ton Rb on the average (average of 5 analyses).

The fourth phase of the intrusion (monchiquites, etc.) is strongly impoverished in rubidium as compared with the rocks of the rest of the intrusive phases. The rubidium content in the monchiquites is 80 g/ton (average of 2 analyses). There are no data in the literature on the rubidium content in the rocks of the lamprophyre series, which includes monchiquites.

The average rubidium content in gabbro, according to E. Horstman [10], is 30 g/ton Rb. The relatively high Rb content in the monchiquites is quite natural, for they contain 1.3% potassium while gabbroids, according to Daly [6], contain only 0.74%. (Potassium in monchiquites was determined volumetrically*).

To compute the average rubidium content in the Lovozero massif it is necessary to determine the areal distribution and thickness of the rocks in the individual intrusive complexes.

According to these data, the rocks of phase I constitute 3% (by volume) of the massif, the rocks of phase II 80%, and those of phase III 17%.

Hence the average rubidium content in the massif is 210 g/ton Rb, which is considerably lower than the average content of 440 g/ton Rb in nepheline syenites in general, given by V. M. Goldschmidt [9].

The calculated average content of Rb and the K/Rb ratios in each intrusive phase are listed in Table 3**.

Table 3

Average Potassium and Rubidium Content in the Rocks of the Lovozero Massif

Intrusive phase	Rocks	Potassium content		Rubidium content		K/Rb
		number of analyses	K, %	number of analyses	Rb p.p.m.	
I	Poikilitic and other nepheline syenites	13	3.91	14	140	280
II	Lujavrites, foyaites, urtites	40	4.13	22	205	200
III	Eudialyte and porphyritic lujavrites	10	3.95	13	230	170
IIIA	Poikilitic sodalite syenites and tawites	7	2.50	5	145	170
	Average		4.09		210	195

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*The method was developed by Yu. P. Trusov and O. F. Mironova in the V. I. Vernadskii Institute of Geochemistry and Analytical Chemistry.

**The K/Rb ratio was calculated on the basis of a large number of sufficiently representative silicate analyses for potassium taken from the literature [1, 2, 7]. The figures for K and Rb are more reliable when obtained from analysis of the same sample.

Table 3 does not give the data for monchiquites, because monchiquite dikes in the massif are too few to justify a generalization concerning the geochemistry of rubidium in the lamprophyre dike series.

It should be noted that the rocks of the first intrusive phase have a much higher K/Rb ratio than the rocks of the later phases. This agrees with the data of those investigators [1, 2] who consider poikilitic and other nepheline syenites as the oldest alkalic complex.

Table 3 shows that poikilitic sodalite syenites and tawites have low K/Rb ratio and this confirms the opinion of Gerasimovskii and O. A. Vorob'eva [1, 2] that the sodalite rocks and the eudialyte lujavrites of the third phase are genetically related and that the latter are younger.

On the other hand, the great difference in the K/Rb ratios in the sodalite syenites (170) and the poikilitic and other nepheline syenites (280) can hardly be reconciles with Eliseev's view that the sodalite syenites are as old as the rocks of phase I.

In spite of the constancy of the K/Rb ratio in sodalite rocks and eudialyte lujavrites, the former contain considerably less potassium and rubidium than the eudialyte lujavrites (see Table 3). The lower potassium and rubidium content in sodalite syenites and tawites may evidently be explained by the fact that the main mass of potassium and rubidium at the time of formation of sodalite-bearing rocks was bound in potassium feldspars and in nepheline of eudialyte lujavrite and the remaining melt strongly enriched in sodium and volatiles (Cl, F, S, H_2O), but impoverished in potassium and rubidium.

Thus, these K/Rb ratios confirm the age sequence of the intrusive phases given above.

The average K/Rb ratio for the massif is 195 (Table 3). This figure is lower than the figures for igneous rocks given by Taylor et al. [11] and by Horstman [10] (240 and 270, respectively).

Summary

1. The average rubidium content in the Lovozero alkalic massif is 210 g/ton Rb.

The rubidium content in nepheline syenites of the massif increases regularly from 140 g/ton Rb in the rocks of the first intrusive phase to 230 g/ton Rb in the rocks of the third intrusive phase.

2. The K/Rb ratio in the nepheline syenites of the massif decreases regularly toward the end of the magmatic cycle from 280 in the first phase to 170 in the third. The average K/Rb ratio for the massif is 195.

3. The low K/Rb ratio (170) in the poikilitic sodalite syenites and tawites confirms their relationship to the third intrusive phase.

4. The rubidium content in the lujavrite-foyaite-urtite (phase II) complex is 205 g/ton Rb, the rocks richest in rubidium being the feldspathic varieties of nepheline syenite, and the poorest the essentially nepheline rocks (urtites).

5. The youngest rocks of the massif, the poikilitic nepheline syenites and tawites, and also the monchiquites of the dike series, are poor in rubidium (145 and 80 g/ton Rb, respectively).

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THE RADIOMETRIC METHOD OF EXPLORATION FOR PETROLEUM AND GAS DEPOSITS

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(ABSTRACT)

Samples of the surface layer of rocks at a depth of 25 cm on the gas-petroleum deposit Kizyl-Kum and the underground structure Gekcha (Western Turkmenia) were selected and analyzed to determine the cause of the typical distribution of intensity of γ-radiation which is observed on several oil-bearing areas.

The results of analyses showed that the distribution of γ-radiation is related to a parallel change in the concentration of all radioactive elements (U, Ra, Th and K).

Radon is contained in oil gases in quantities not sufficient to cause the observed change of intensity of γ-radiation along the outline of the deposit.

These results bear witness of the fact that on the above structures the hypothesis of a relation between the γ-radiation, being typical of several oil-deposits, and the precipitation of radium or of their daughter products on the outline of the oil-bearing bed is not confirmed.

The first attempts at radiometric exploration for petroleum were made in the USSR by L. N. Bogoyavlenskii in 1924. The oil pools of the Maikop region revealed high values of "strongly penetrating radiations" [1].

Later investigations did not confirm the existence of "strongly penetrating terrestrial radiations" on whose modification in passing through petroliferous beds Bogoyavlenskii based his prospecting method. As a result, his work lost its significance and received no further development.

In the late 40's of our century, some investigators in the U. S. A. (Lundberg et al. [2, 3]) revived radiometric methods of exploration for oil. It was shown empirically that petroliferous structures are marked by lower intensity of gamma-radiation from the earth's surface as compared with the average. Moreover, it appeared that the boundary of a gas-oil deposit was characterized by a higher than average gamma-activity. Beginning in 1939, carborne and airborne radiometric surveys for oil were initiated in the U. S. A. *

The observed anomalies may result from the distribution of radioactive elements reflecting:

1) the lithology and facies composition of the surface layer of rock and

2) the enrichment or impoverishment of individual areas in one or several radioactive elements due to their migration caused by physicochemical processes, possibly related to the gas and oil deposits at depth.

Lundberg and other investigators [2-4] suggested there is a probability of accumulation and deposition of radium brought from the depths on the boundary of a gas-oil deposit or of a high concentration of radon diffusing with natural gas.

Because of the great practical importance of any method which would locate deep-seated oil pools directly (even if it is not very effective) the radiometric method attracted attention in our country also.

The very first tests, conducted by the Petroleum institute under the direction of F. A. Alekseev, confirmed the existence of negative gamma radiation anomalies over petroleum and gas deposits in a number of petroliferous localities of the USSR [5-9].

To determine the causes of these anomalies, it was necessary to study the distribution of the radioactive elements, the source of gamma-rays, over the survey areas. For this purpose, the Institute of Geochemistry and Analytical Chemistry sent a group of workers under the leadership of N. G. Morozova which took part in the field work by Alekseev's Laboratory and investigated the radioactivity of waters and gases in the structures with characteristic anomalies. The group collected samples of soils and rocks of the surface layer penetrated by gamma-rays and determined their content of radioactive elements.

To determine the nature of gamma-ray anomalies connected with gas and oil deposits, several areas containing known and possible petroliferous structures and giving clear gamma-ray anomalies were selected. It should be noted that the range of variation in gamma-activity along profiles is slight and does not amount to more than 30% of the average activity along the profile, which is characteristically low in sedimentary rocks.

Brief geological descriptions of the selected areas, the results of radiometric surveys and an account of the distribution of radioactive minerals in the rocks along selected profiles are given below. The geological data are based on field work. The results of airborne and carborne surveys were contributed by Prof. Afanas'ev's Laboratory.

The chemical analyses of the samples were made by B. V. Krasev, E. V. Babicheva and A. M. Dorina, and the radiochemical determinations by K. G. Kunasheva and A. P. Novitskaya. The present article is based on field observation and on part of the laboratory data.

The results of radiochemical analyses are given on the profiles in activity units of gamma radiation emitted by radium, the thorium series and potassium contained in the rocks.

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*It should be recalled that gamma radiation registered by an instrument is due to the radioactivity of a surface layer 30 cm thick.

INVESTIGATIONS IN WESTERN TURKMENIA

Two structures were selected for investigation in Western Turkmenia: the natural gas deposit of Kizyl-Kum, with known boundaries of bas-bearing beds, and 2) the potentially productive Gekcha structure outlined by a negative gamma-radiation anomaly characteristic of petroliferous structures.

The Kizyl-Kum Natural Gas Deposit

The outcropping rocks which outline the structure in the north and southwest are Khazarian alluvial-deltaic deposits. In the west, the beds of Khazarian age are covered by Novocaspian marine sediments. The structure itself is overlain by late Khvalynian marine deposits. On the surface the Novocaspian and late Khvalynian marine deposits are represented by sands reworked by wind whose gamma-activity, according to data of airborne and carborne surveys, is 6 - 7 millicuries/hour. The variation of gamma-radiation along the traverses amounts to 1 - 2 millicuries/hour.

It has been shown by carborne survey that the gamma radiation from the eolian sands is less than from the underlying marine deposits.

Field work gave a characteristic picture of low gamma-activity over the productive crest of the structure. Profile MN was selected for chemical and radiochemical determinations of the concentration of radioactive elements in the surface rocks. The results of the determinations are presented in Table 1, where the content of radioactive elements is given in curies per gram of rock and (for convenience in graphic comparison) the contribution of each element to gamma-radiation in millicuries/hour.

It was assumed in the calculations that gamma radiation emitted at the surface by 0.01% U in equilibrium with its decay products amounts to 50 millicuries/hour and that the ratio of the gamma-activities of equal weights of U, Th and K is $U_\gamma : Th_\gamma : K_\gamma = 1:0.43:0.0002$ (experimental data obtained by V. L. Shashkin and associates [10] for a 10 cm layer).

Fig. 1 presents curves of gamma-activity plotted on the basis of carborne survey (curve I) and measurement of gamma-activity of samples by the counter LS (curve II) as well as calculated gamma-activity curves for potassium and thorium ($K_\gamma + Th_\gamma$), and the curves of total gamma activity of U, Ra, Th and K ($\Sigma(U_\gamma + Th_\gamma + K_\gamma)$; $\Sigma(Ra_\gamma + Th_\gamma + K_\gamma)$). In plotting the curves of total activity, to avoid errors possible in the determination of small concentrations of radioactive elements, the calculation of the gamma activity due to the uranium series was made in one case on the basis of chemical analyses for U on the assumption of equilibrium in the series, and in the other, on the basis of radiochemical analysis for radium.

A detailed examination of Fig. 1 shows that in spite of the characteristic variation in gamma activity along profile MN, across the natural gas structure, the "halo" effect is caused by the general distribution of the radioactive elements along the profile and not by a contribution from radium alone. Radium is in equilibrium with uranium (within the accuracy of chemical and radiochemical analysis).

Thus, the pattern reflects lithological-facies characteristics of the surface rocks rather than geochemical processes connected with the gas-oil deposit at depth.

Table 1

Content of U, Ra, Th and K in the Surface Samples Along Profile MN at the Kizyl-Kum Natural Gas Deposit

Sample number	K $n \cdot 10^2$ g/g	K^{40} $n \cdot 10^{12}$ curies/g	Th		Ra	U		Th:U	Share of activity (millicuries/hour) Calculated				Total gamma activity		
			$n \cdot 10^{12}$ curie/g	$n \cdot 10^6$ g/g	$n \cdot 10^{12}$ g/g	$n \cdot 10^{12}$ curie/g	$n \cdot 10^6$ g/g		K_γ	Th_γ	U_γ	Ra_γ	$Th_\gamma + K_\gamma$	$\Sigma_{U_\gamma} + Th_\gamma + K_\gamma$	$\Sigma'_{Ra_\gamma} + Th_\gamma + K_\gamma$
1104/75	1,49	18,3	0,67	4,20	0,4	0,79	1,65	2,62	1,49	0,90	0,82	0,60	2,39	3,21	2,99
1105/76 (depth)	1,53	18,8	—	—	—	0,91	1,90	—	1,53	—	0,95	—	—	—	—
1103/74	1,61	19,9	0,59	3,75	0,6	0,63	1,30	2,84	1,61	0,81	0,65	0,90	2,42	3,07	3,32
1100/71	1,79	22,0	0,76	4,80	0,8	1,61	3,35	1,45	1,79	1,03	1,68	1,20	2,82	4,50	4,02
1101/72 (depth)	1,65	20,3	—	—	0,5	0,96	2,00	—	1,65	—	1,00	0,75	—	—	—
1097/68	1,53	18,8	—	—	—	0,51	1,05	—	1,53	—	0,52	—	—	—	—
1096/67	1,52	18,7	—	—	0,7	1,06	2,20	—	1,52	—	1,10	1,05	—	—	—
1092/63	1,74	21,4	0,67	4,20	0,7	0,75	1,55	2,50	1,74	0,90	0,77	1,05	2,64	3,41	3,69
1091/61	1,52	18,7	0,60	3,80	1,0	1,01	2,10	1,81	1,52	0,82	1,05	1,50	2,34	3,39	3,84
1091/62 (depth)	1,72	21,0	0,79	5,00	0,5	0,75	1,55	3,31	1,72	1,07	0,77	0,75	2,79	3,57	3,54
1086/57	1,47	18,1	0,59	3,70	0,6	0,63	1,80	2,84	1,47	0,80	0,65	0,90	2,27	2,92	3,17
1084/55	1,32	16,2	0,67	4,20	0,5	0,87	1,80	2,32	1,32	0,90	0,90	0,75	2,22	3,12	2,97
1079/50	1,52	18,7	0,59	3,75	—	0,67	1,40	2,64	1,52	0,81	0,70	—	2,33	—	—
1077/48	1,49	18,3	0,71	4,50	0,6	0,89	1,85	2,50	1,49	0,97	0,92	0,90	2,46	3,38	3,36
1032/3	1,68	20,6	0,40	2,50	0,5	0,65	1,35	1,92	1,68	0,54	0,67	0,75	2,22	2,89	2,97
1033/4	1,57	19,3	0,52	3,25	0,4	0,75	1,55	2,12	1,57	0,70	0,77	0,60	2,27	3,04	2,87
1037/8	1,34	16,4	0,76	4,80	0,5	0,82	1,70	2,82	1,34	1,03	0,85	0,75	2,37	3,22	3,12
1038/9 (depth)	1,53	18,8	0,67	4,15	1,0	0,60	1,25	3,42	1,53	0,89	0,62	1,50	2,42	3,04	3,92
1045/16	1,80	21,9	0,77	4,87	0,9	1,28	2,65	1,84	1,80	1,05	1,32	1,35	2,85	4,17	4,20
1052/23	1,72	21,2	0,84	5,30	0,9	1,13	2,35	2,30	1,72	1,14	1,17	1,35	2,86	4,03	4,21
1061/32 (depth)	1,33	16,3	0,73	4,60	0,6	0,70	1,45	3,28	1,33	0,99	0,72	0,90	2,32	3,04	3,97
1062/33	1,53	18,8	0,80	5,05	0,7	1,30	2,70	1,85	1,53	1,09	1,35	1,05	2,62	3,97	3,67
1072/43 (depth)	1,34	16,4	—	—	—	1,20	2,50	—	1,34	—	1,25		—	—	—
Average									1,57	0,9	0,93	0,97	2,48	3,45	3,42

NOTE: Comma represents decimal point.

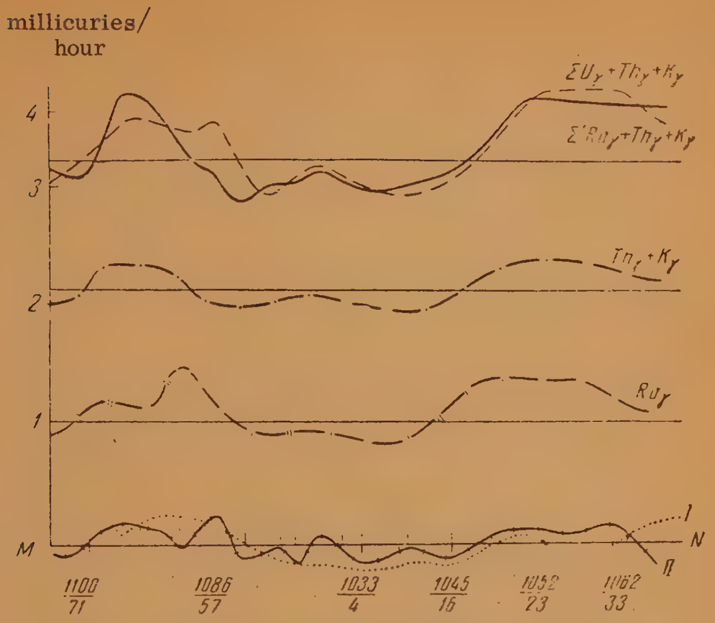

Fig. 1. Distribution of gamma activity along profile MN (Kizyl-Kum deposit)

In all diagrams (1, 2, 3, 4) the horizontal scale = 1 : 1,000,000, vertical scale - arbitrary

The Gekcha Deposit

The Gekcha structure is a buried anticline. The surface of the area is a plain of rather uniform lithology. The southern end of the structure exhibits typical erosional features produced by intermittent streams which dry up in summer. No petroleum indications are known within the boundaries of the structure. Carborne radiometric survey shows minimum values of gamma activity over the western limb and the crest of the structure parallel to its axis. The absolute decrease in the intensity of gamma radiation in the anomaly area does not exceed 0.75 – 1.0 millicuries/hour. A detailed study of the anomaly was made along profiles AB, CD and EF, which cross the central part of the structure.

Figs. 2, 3 and 4 represent the distribution of gamma-activity along the profiles AB, CD and EF crossing the possibly petroliferous Gekcha structure as recorded by carborne radiometric survey and the data of chemical and radiochemical analyses.

The curve of total gamma activity calculated from the content of radioactive elements (for profiles AB and CD) parallels the curve recorded by carborne survey. In the case of profile EF the non-correspondence of the curves is due to thorium and uranium. However, the main question of the hypothetical role of radium in the formation of negative gamma radiation

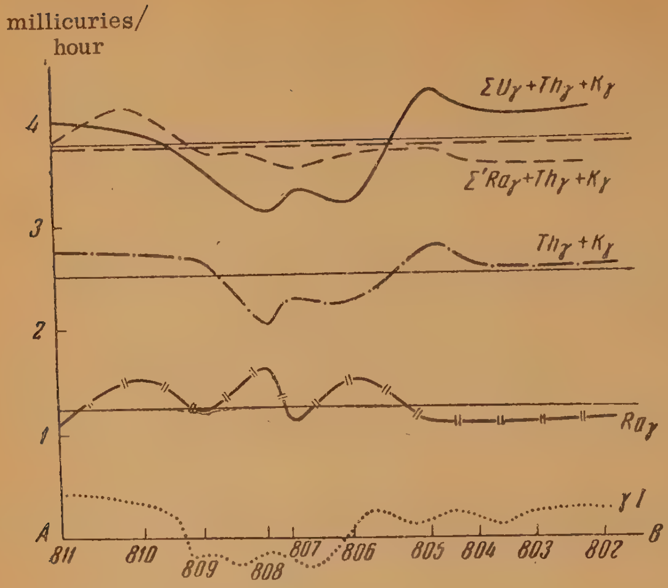

Fig. 2. Distribution of gamma activity along profile AB (Gekcha deposit)

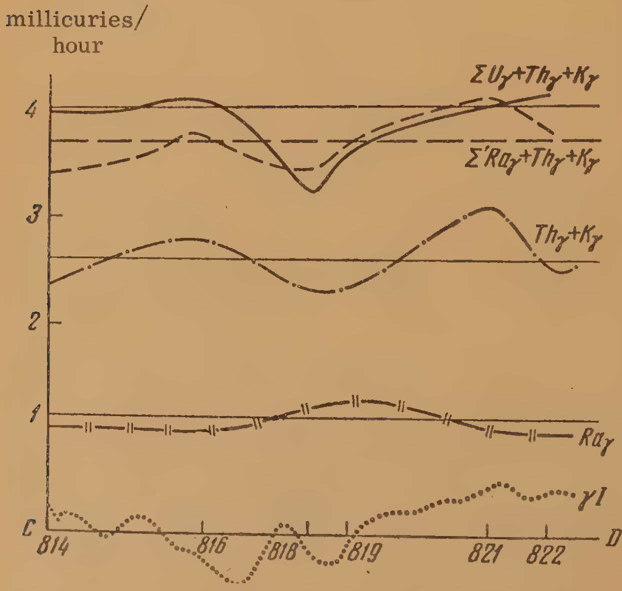

Fig. 3. Distribution of gamma activity along profile CD (Gekcha deposit)

anomalies over petroliferous structures is clearly answered. Radium in this case does not play such a role.

During field work, samples of water from oil wells and from the surface were taken in the Middle Povolzh'ye in the areas of the Korobkovo and Frolovo oil fields of the Petrushensk structure and in Western Turkmenia at the Kum-Dag oil field and the Boya-Dag and Gekcha structures. Radon, radium and uranium were determined in the samples, but no characteristic regularities confirming the hypothesis of the American investigators were found.

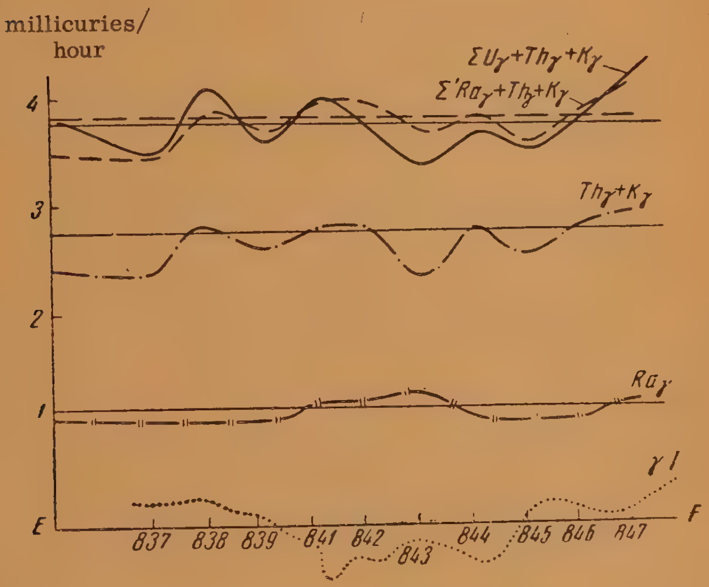

Fig. 4. Distribution of gamma activity along profile EF
(Gekcha deposit)

RADIOACTIVITY OF PETROLEUM GASES

In connection with the statements concerning the affinity between hydrocarbons and radioactive elements and the possible migration of the latter towards the surface with natural gas, it appeared worthwhile to determine the content of radioactive emanations in natural gas. A series of analyses were made of natural gas from gas wells and of the gas associated with petroleum in the Korobka gas and oil deposit of the Archeda petroleum region.

The results of the analyses are given in Table 2.

Table 2

Radioactivity of Natural Gases

No. of well and description of sample	Perforation spacing	Content of emanations curie/1		Oil-gas horizon
		Rn	Tn	
Korobka gas-oil deposit				
3, gas associated with oil	1754—1760		$1.1 \cdot 10^{-12}$	Stalinogorsk (sandstone)
17 "	1728—1742	$2.04 \cdot 10^{-12}$	0	"
36 "	1727—1745	$7.40 \cdot 10^{-12}$	$2.15 \cdot 10^{-13}$	"
23 "	1719—1738	0	0	" *
13, gas condensate	1725—1734	0	0	"
30, " petr. gas		0	0	"
36, Jurassic gas	205—208	$4.04 \cdot 10^{-11}$	0	Dry gas
8bis "		$4.60 \cdot 10^{-11}$	0	"
9 "		$11.12 \cdot 10^{-11}$	0	Dry gas**
0 "		$4.50 \cdot 10^{-11}$	0	"
Archeda petroleum deposit				
4, gas associated with oil	1011—1013	$1.42 \cdot 10^{-11}$	0	Stalinogorsk
77 "	1710—1716	$7.60 \cdot 10^{-12}$	0	Devonian
38 "	1008—1011	$3.88 \cdot 10^{-12}$	0	Stalinogorsk
18 "	1011—1013	$1.60 \cdot 10^{-12}$	0	Tournaisian
93 "	1404—1406	$1.03 \cdot 10^{-11}$	0	Devonian
71 "	1020—1021	$8.43 \cdot 10^{-12}$	0	Tournaisian

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*Gas and oil exude strong H_2S odor.

**Before measurements air was blown through the well for 10 min.

According to Table 2, the content of Rn and Tn in natural gas is lower by one order of magnitude than their average content in soil air ($2 \cdot 10^{-10}$ curies/liter) for the normal average concentrations of the parent elements in the rocks.

The presence of Tn in the gases of wells 3 and 36 (Korobka deposit) may be explained by the presence of MsTh or ThX in petroleum.

Thus natural gases are not by themselves responsible for anomalous gamma activity.

This may be confirmed by a quantitative estimate of the role of Rn in increasing gamma activity over the surveyed areas if it is assumed that it rises from depth with diffusing natural gases. Let us recall that the main emitters of gamma rays, the daughter products of radon, Ra (B + C), are practically in equilibrium with it, for steady state is attained after 3 hours, and therefore exists permanently under natural conditions.

If 1 cm^3 of rock contains ρ_r of matter and its porosity coefficient is p, then with the concentration of Rn in natural gas being ϵ (curie/cm^3), the radon content in 1 cm^3 of rock will be ϵp and the concentration of Rn per gram of rock will be $C_{Rn} = \frac{\epsilon p}{\rho}$ curies/g.

The intensity of gamma radiation from C_{Rn} corresponds to the content:

$$C_{Ra} = \frac{\epsilon p}{\rho} \text{ g/g.}$$

The maximum Rn content was found in well 9 of the Korobka deposit (Table 3) and equals $1.1 \cdot 10^{-10}$ curies/liter or $1.1 \cdot 10^{-13}$ curies/cm^3. This corresponds to the radium content in modern soils with $\rho = 0.4$ and $\rho = 2$.

The concentration of radon $C_{Ra} = \frac{1.1 \cdot 10^{-13} \cdot 0.4}{2} = 2.2 \cdot 10^{-14}$ g/g, and this, with the radon clarke in sedimentary rocks being 10^{-12} g/g, amounts to 2%. This contribution to gamma activity from radon is beyond the sensitivity of existing instruments, and therefore the hypothesis of the role of emanations diffusing with natural gas in the formation of halos cannot be accepted as a working hypothesis.

Summary

1. In a number of cases negative gamma radiation anomalies characteristic of gas-oil localities have been observed. These anomalies correspond entirely to the distribution of radioactive elements (U, Ra, Th and K) in the surface soil layer (25 cm), and this confirms their objective existence.
2. The observed anomalies have small amplitudes (from 25 to 30% of the average gamma activity along a profile) and negligible absolute values ($3 \div 7$ millicuries/hour).
3. The hypothesis of a number of authors that radium plays a specific role in the formation of negative gamma radiation anomalies and "halos" has not been confirmed by an investigation of the Kizyl-Kum gas and petroleum structure and of the possibly petroliferous Gekcha structure.
4. No predominance of any one of the radioactive elements which might determine the character of distribution of gamma radiation has been

observed, and so no other geochemical hypothesis can be advanced. Most probably the variations in gamma activity are caused by lithofacies or structural-morphological peculiarities of petroliferous regions [11, 12].

5. The gamma radiation from the radioactive emanations contained in natural gases constitutes a negligible fraction (~2%) of the gamma radiation emitted by radioactive elements (with clarke concentrations in soils). Natural gases diffusing from an oil pool to the surface play no role in the concentration of the daughter products of radon at the surface along the boundary of a gas-petroleum deposit and are not responsible for "halos".

6. The accumulation of new radiometric data should help to solve the problem of anomalies in petroliferous regions.

In conclusion, the authors express their gratitude to Professor F. A. Alekseev and his group for helping in this research and for providing necessary materials.

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DIFFUSION OF ARGON IN SYLVITE

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(ABSTRACT)

Experimental results of measurements of radiogenic argon diffusion constants (D) at temperature 20—700° C and its activation energy (E) and of electrical conductivity in the frequency range 0—20 mgc and its activation energy (E) are given for two specimens of sylvite. The mechanism of radiogenic argon diffusion is found to differ from that of electrical conductivity and self-diffusion of K^+. In the impurity conduction band E = 47 kcal/mole, E = 22—30 kcal/mole. The diffusion constant extrapolated to 300° K is found to be 10^{-30} cm^2/sec. As the most probable mechanism of radiogenic argon diffusion the diffusion across associated pair vacancies and Schottky defects is discussed. For one of the sylvite specimens low-temperature desorption-type argon losses were found probably due to the mosaic crystal-structure.

To evaluate further possibilities of the argon method for the determination of absolute ages of geological formations, it is essential to know the mechanism of migration of radiogenic argon atoms in the mineral lattices. Sylvite, an isometric mineral, is the most suitable material for a preliminary investigation of this kind. In references [1, 2], devoted to the diffusion of radiogenic argon in sylvite, the diffusion coefficient was not measured by direct physical methods and the energy of activation was not determined at all, while in reference [3] the theoretical discussion of the problem was not documented by experimental data. In the present paper, the experimental values of the diffusion coefficient and the energy of activation for radiogenic argon obtained for two samples of Solikamsk sylvite are compared with the experimental values of conductivity and dielectric loss, whose mechanism is well known.

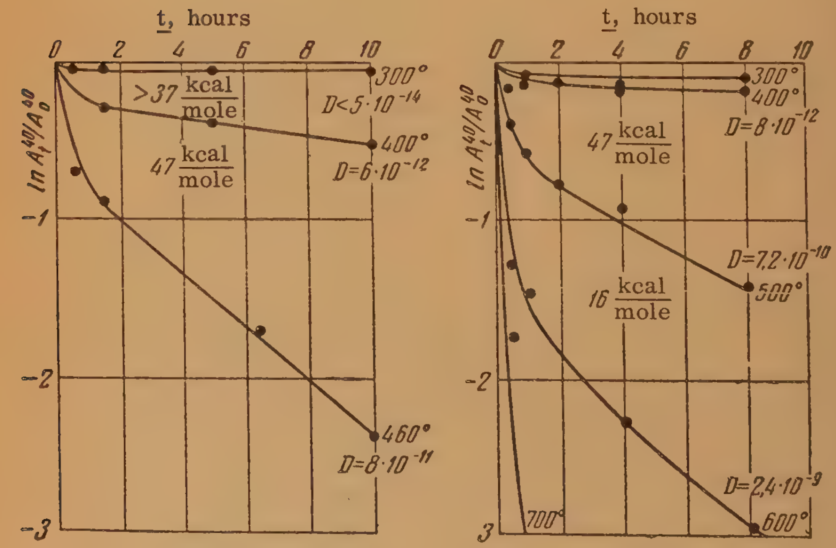
To determine the diffusion coefficients D and the activation energies E, 2g samples (of "pink" and "red" sylvite) were heated at a given temperature for different periods of time. The radiogenic argon remaining in the samples was measured on a mass spectrometer by the method of isotope dilution [4]. The results are given in Fig. 1 (a -- red sylvite, b -- pink sylvite). The duration of heating is plotted on the abscissae, and the temperature is marked on the curves. The values $\ln \frac{A_t}{A_0}$ are plotted on the ordinates (A_t is the content of radiogenic argon in 10^{-9} mm³/g at STP after heating for a given time, and A_0, the initial content of radiogenic argon). For the red sylvite (0.053 - 0.105 mm fraction), A_0 is 0.170×10^{-9} mm³/g; for the pink (0.210 - 0.420 mm fraction) it is 0.300×10^{-9} mm³/g.

By comparing the experimental curves with the theoretical, computed by the formula,

$$\ln\frac{A_t}{A_0}=\frac{6}{\pi^2}\sum_{n=1}^{\infty}\frac{1}{n^2}e^{-\frac{\pi^2 n^2}{r^2}Dt}, \tag{1}$$

(r = average radius of the grains) the values of the diffusion coefficients were determined for each temperature of heating. These values are given in Fig. 1 on the corresponding curves. For each pair of values of D the activation energy was calculated by the formula

$$D = D_0 e^{-\frac{E}{RT}} \tag{2}$$



a b

Fig. 1. Liberation of radiogenic argon from sylvites:

a -- red sylvite, b -- pink sylvite

he values of E are also given in Fig. 1. It will be seen from Fig. 1a that e diffusion of radiogenic argon occurs in the temperature interval 300 - 0°C (at 500°C all argon is liberated during the first hour of heating). The tivation energy in this temperature interval remains approximately con- ant and equals 37-47 kcal/mole (~ 2 ev). A more complicated case is esented by the pink sylvite (Fig. 1 b). First, there is low temperature ss of argon at 300°C, evidently due to its desorption from the mosaic undaries. This phenomenon has already been described by us for micas, auconites and feldspars [5, 6, 7]. Second, while in the interval 400- 0°C the activation energy is of the same order as for red sylvite, in the terval 500-600°C, it decreases to 16 kcal/mole (~ 0.7 ev), which con- adicts the generally accepted theory of thermal activation. It must be sumed that in the second temperature interval the mechanism of diffusion argon changes and is different at 600°C. It is not permissible, there- re, to calculate activation energy using values of D corresponding to dif- rent mechanisms of diffusion. Between the D curves for 500°C and 600°C ig. 1 b), there must lie a boundary curve with a minimum slope indicat- g the appearance of the new mechanism of migration of radiogenic argon.

Taking the value of the diffusion coefficient at 400°C as $6 \cdot 10^{-12}$ cm^2/sec, d of the activation energy as 47 kcal/mole, we can compute with the aid formula (2) the diffusion coefficient and activation energy for 300°K. It uals 10^{-30} cm^2/sec. These values of the diffusion coefficient and activa- n energy insure the preservation of radiogenic argon through geologic ne even at temperatures of 100°C.

It is known that, in the alkali halide crystals, self-diffusion and conduc- ity obey the Nernst-Einstein relation and the activation energy of these ocesses decreases with decreasing temperature due to the effect of im- rities [8, 9]. This suggested to Curtis and Reynolds [3] that the diffusion radiogenic argon in sylvite crystals occurs via vacancy pairs of the

$\boxed{\;|\;\mathrm{Cl}^-}$ type and is characterized by activation energy of the order of 1

(23 kcal/mole). The values of activation energy obtained by us are ice as high for both sylvites. Evidently the diffusion of radiogenic argon es not obey the Nernst-Einstein relation and its mechanism is different om that of self diffusion of alkali ions.

To prove this, we investigated the dependence of conductivity on fre- ency in both sylvites at different temperatures. The measurements were ade with a Q-meter of the KV-1 type in a coaxial condenser of special nstruction (Fig. 2). The sample (6) (usually < 0.05 mm fraction) was ured between the inner and outer electrodes (1 and 2) and the condenser vered with a lid (4) provided with a hole for the thermocuple (5). Parts 2 and 4 were made of stainless steel of low thermal conductivity. The sulation between the electrodes consisted of two porcelain rings (3) oled by running water. This prevented variation in the insulating proper- s of porcelain at high temperatures. The condenser was heated in the rizontal position by means of an electric furnace.

The factors $Q = \tan^{-1} \delta$ were obtained for the frequency interval from kilocycles to 20 megacycles. The value of conductance g was calculated om the formula

$$q = \underline{b \tan} \delta, \tag{3}$$

ere b is resistivity and δ is the loss angle.

Fig. 3 (a, b) shows the experimental curves for the red and pink sylvites,

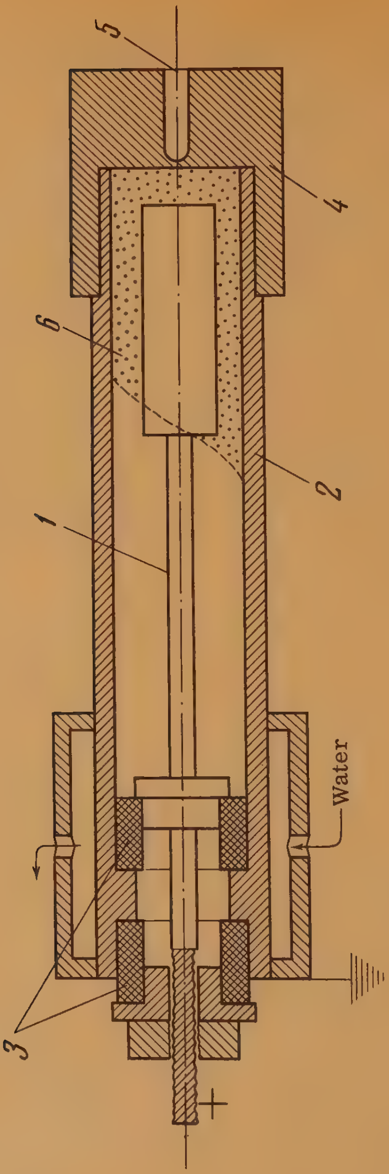


Fig. 2. Diagram of the condenser used in measuring electrical properties of minerals

1 – inner electrode, 2 – outer electrode, 3 – porcelain rings, 4 – lid, 5 – thermocouple well, 6 – sample

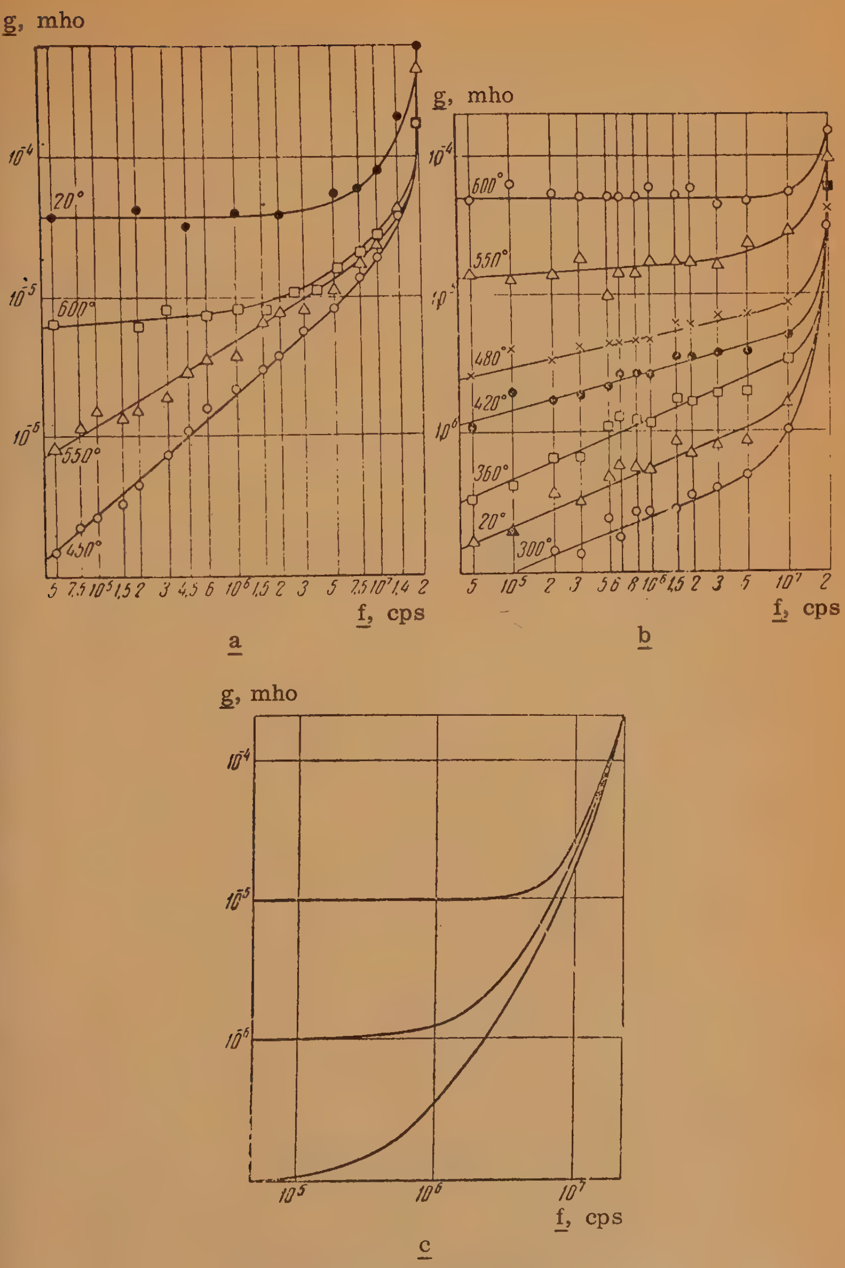


Fig. 3. Experimental conductivity curves

a - for red and b - for pink sylvites, c - theoretical curves respectively. It will be seen that the factor of thermal activation affects mainly the low and medium frequency parts of the curves, while the high frequency segments coalesce into a single curve. The theory of dielectrics [10] gives the following expression for the effective value of current i_α passing through a dielectric possessing relaxation effects besides the intrinsic conductivity:

$$i_a = \left(g_{\text{intr}} + \frac{\omega^2\theta^2}{1 + \omega^2\theta^2} g' \right) U. \quad (4)$$

Here g is intrinsic conductivity, U, the effective value of applied field of angular frequency ω, and g' and θ are constants characterizing the polarization effects in the dielectric related to relaxation time. Fig. 3 (c) shows calculated curves constructed according to formula (3), with g' and θ = const. and three different g_{intr}/g' ratios. Comparing Fig. 3 (c) with Fig. 3 (a and b), we see that thermal activation in the investigated samples leads also to a change in the g_{intr}/g' ratio; i.e., it affects the intrinsic conductivity of sylvite. To determine the character of this conductivity, we subjected the samples to the action of strong magnetic fields (up to 25,000 oersteds) in a special condenser, and also to the action of CuKα radiation (for 10 - 15 minutes). The conductivity was not affected by this, although strong luminescence was induced by the x-rays.

It follows that the conductivity in sylvites is not due to the migration of electrons but is purely ionic. The curves showing the dependence of conductivity of red and pink sylvites on the temperature at a constant frequency (100 kilocycles) are given in Fig. 4. These curves are drawn on the basis of the data of Fig. 3, a and b, and in accordance with established practice, the values 1/T are plotted on the abscissae and the logarithms of

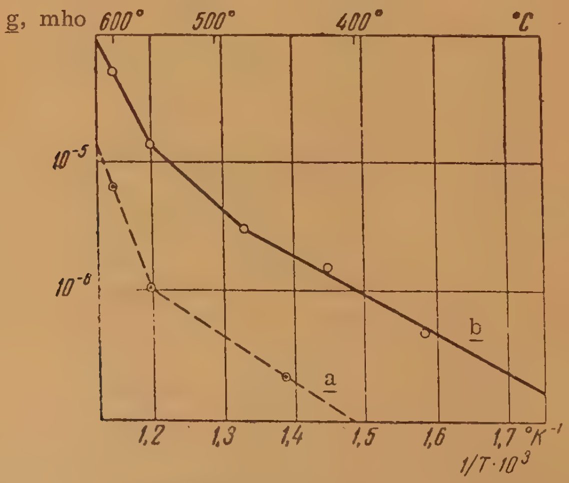


Fig. 4. Temperature dependence of sylvites at 100 cps frequency

Note: Comma represents decimal point.

conductivity, on the ordinates. These curves consist of straight segments and possess properties determined by Mapother, Crookes and Maurer in [11]. These authors showed that ionic conductivity in alkali halides is due mainly to the migration of positive ions through vacancies which form at low temperatures, because of the presence of bivalent impurities, and at high temperatures, because of the formation of Schottky defects. Both curves of Fig. 4 show a characteristic knee at 550°C noted in reference [11] as the boundary between the extrinsic region and the region of conductivity via thermal defects of the Schottky type. The curve for pink sylvite has a second knee (at 480°C), indicating a more complex structure of the impurity zone.

The curves of Fig. 4 do not permit any conclusions to be made concerning the energy of activation E of the different types of conductivity because of the distorting effect of the second member of the formula (4). Moreover, we showed that in our case intrinsic conductivity plays the principal role. Therefore, it was necessary to make further investigations of conductivity using direct current, for in this way the value of intrinsic conductivity can be obtained directly from the relation of the form

$$\gamma = \gamma_0 e^{-\frac{E}{RT}} \tag{5}$$

where γ is specific conductance.

These measurements were made in the condenser (Fig. 2) with a megohmmeter MEG-8 or, in case of low resistance, with a voltmeter and ammeter of 0 - 0.5 amp range. The results of the measurements are given in Fig. 5 (a, b). For comparison, the same diagrams give the diffusion curves. The values of activation energy are marked at the corresponding segments of the curves. We see that the diffusion of radiogenic argon occurs in both sylvites up to the knee in the conductivity curves (550°C), i.e. in the extrinsic region. The activation energy of diffusion (47 kcal/mole) in this temperature interval is considerably greater than the activation energy of conductivity for the red (30.0 kcal/mole) and pink (22.4 and 37.5 kcal/mole) sylvites. The additional knee on the conductivity curve of pink sylvite (Fig. 5 b) does not, evidently, affect the value of the diffusion coefficient. It is characteristic also that in the red sylvite, containing a considerable amount of bivalent impurities, iron and calcium, the radiogenic argon is liberated completely in the extrinsic region.

In the chemically purer pink sylvite, argon is liberated before and after the temperature of 550°C is attained. We have already seen that in the interval between 550°C and 600°C the activation energy of diffusion decreases sharply as compared with the 400-500°C interval (from 47 to 16 kcal/mole).

This change can be explained if it is assumed that the activation energy of diffusion remains constant to the boundary of the extrinsic region (point "a", Fig. 5 b). Then, as we assumed earlier, the diffusion coefficient must decrease to the point "c" corresponding to the liberation of argon in the region of self-diffusion at a given temperature.

This value must be small, and we take it as being equal to the limit of sensitivity of the apparatus. If this assumption is not made, the activation energy of diffusion for the 550-600°C interval would be negative (straight line a-b, Fig. 5), which is not so. It follows that the activation energy of diffusion of radiogenic argon is greater than that of conductivity even in the self-diffusion region.

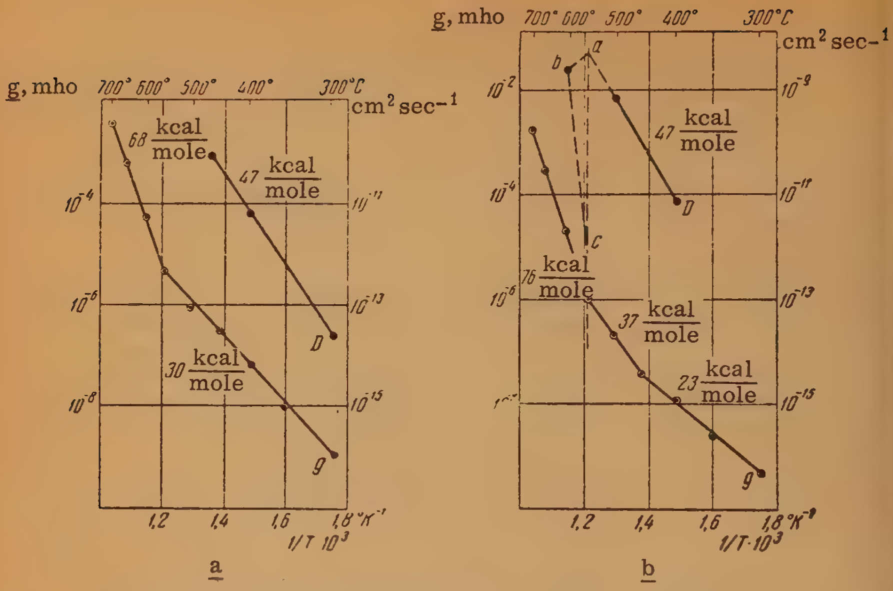


Fig. 5. Temperature dependence of intrinsic conductivity

a – red sylvite, b – pink sylvite

Note: Comma represents decimal point.

Therefore, the mechanism of diffusion of radiogenic argon is not identical with the mechanism of either impurity or intrinsic ionic conduction in a crystal. We have no direct experimental proof that the migration of radiogenic argon occurs via vacancies of $\boxed{K^+ \mid Cl^-}$ type, as supposed by Curtis and Reynolds [3]. This may be taken, however, as a working hypothesis if a number of additional assumptions are made concerning the activation energy of radiogenic argon diffusion.

The statistical difference between the mechanism of migration of potassium and of argon lies in the fact that wherever in the crystal a $\boxed{K^+}$ vacancy occurs, it is always in the neighborhood of occupied K^+ sites. This is not the case with argon. The activation energy of diffusion of A^{40} must consist of three components:

a) E_1, accounting for the probability of a jump of A^{40} atom through a vacancy pair $\boxed{K^+ \mid Cl^-}$;

b) E_2, accounting for the activation energy of formation of vacancy pairs $\boxed{K^+ \mid Cl^-}$;

c) E_3, accounting for the mobility of the vacancies $\boxed{K^+ \mid Cl^-}$.

Thus, the diffusion of A^{40} must obey a relation of the form:

$$D_A = D_o e^{-\frac{E_1 + E_2 + E_3}{RT}} \tag{6}$$

Let us assume that an A^{40} atom is so structurally barred from the neighboring vacancies that no activation energy will suffice to move it into one of them ($E_1 \rightarrow \infty$), or that, in the absence of bivalent impurities, no vacancy pairs will form ($E_2 \rightarrow \infty$), or, finally, that the vacancies remain stationary ($E_3 \rightarrow \infty$). In all cases the diffusion coefficient of argon will be zero.

According to Curtis and Reynolds' estimate, $E_1 \approx$ 1 ev, and the value obtained by us for the energy of activation of diffusion in the impurity region is $\approx$ 2 ev; therefore, $E_2 + E_3 \approx$ 1 ev.

Assuming this mechanism of diffusion, the jump D at the point "α" (Fig. 5 b) and the knee in the conductivity curve at the same temperature could be explained by dissociation of vacancy pairs $\boxed{K^+ \mid Cl^-}$ followed by the formation of Schottky defects. The fact that the activation energy of diffusion of A^{40} is greater than the activation energy of conductivity might be explained by the probability of adjacent positions of $\boxed{K^+}$ and $\boxed{Cl^-}$.

Summary

1. The mechanism of diffusion of radiogenic argon in sylvite is not identical with the mechanism of their ionic conductivity and self-diffusion of positive ions. The energy of activation of diffusion is greater than the energy of activation of conductivity at the same temperature.
2. There is no reason to expect a decrease in the energy of activation of diffusion of radiogenic argon at low temperatures (below 200° C). If losses of radiogenic argon have occurred in geologic time, they were not due to volume diffusion.
3. Low temperature loss of argon occurs in sylvites by desorption and may be ascribed to the mosaic structure of the crystals.
4. The change from impurity conduction in sylvites to intrinsic conductivity is accompanied by an abrupt change in the diffusion coefficient. It is assumed that the migration of A^{40} atoms occurs via vacancy pairs, this abrupt change may be explained by dissociation of vacancy pairs.

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THE DISTRIBUTION OF LEAD IN SOME GRANITOIDS OF EASTERN TRANSBAIKALIA

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(ABSTRACT)

The lead distribution of some granitoids of Eastern Transbaikalia has been studies, a connection between them and the zinc-lead, molybdenum and tin-tungsten mineralization being assumed. Some tendency for a decrease in lead balance at the expense of feldspars is noted at the transition from granitoids of the zinc-lead zone to granitoids of the tin-tungsten metallogenic zone. Intrusions with which the zinc-lead mineralization is connected are distinguished by a lower lead content compared to magmatic formations with which a connection of the molybdenum and tin-tungsten mineralization is established.

Studies of the distribution of elements in igneous rocks aid in the solution of a number of petrogenetic problems and also provide clues to the degree and type of mineralization of a given magmatic complex.

It appeared worthwhile in the course of an investigation of the geochemistry of lead in the igneous rocks of Eastern Transbaikalia to determine its distribution in the granitoids of the different metallogenetic zones.

Studies were made of the most typical intrusive rocks which, according to the geological data, were responsible for the mineralization. A polymetallic mineralization is believed to be genetically associated with the Klichka quartz diorite, the Shakhtama molybdenum mineralization with the Shakhtama granodiorite and a tin deposit, with the Malyi Soktui granite.

These massifs lie within the boundaries of different metallogenetic zones of Eastern Transbaikalia separated by S. S. Smirnov: the quartz diorites, in the polymetallic zone; the granodiorites, in the molybdenum zone; and the granites, in the tin-tungsten zone.

The oldest rocks in the Klichka deposit are the Lower Paleozoic carbonate and shale beds. They are cut by an intrusion of Variscan granites widely exposed in the region. Alaskites predominate in this complex (350 km^2).

The Variscan granites are transgressively overlain by Lower and Middle Jurassic clastics (conglomerates and sandstones). The Upper Jurassic is represented mainly by intermediate volcanics.

A few small intrusions of quartz diorite and quartz syenites are related to the Kimmeridgian folding. The mineralization at the Klichka polymetallic deposit is related to the quartz diorite.

Intrusive rocks predominate in the structure of the Shakhtama molybdenum deposit. These rocks are of different ages. The oldest are the Upper Paleozoic porphyritic granites of the so-called Verkhne-Udinsk complex. The granitic rocks of this complex are intruded by the granodiorite of the Shakhtama type (300-350 km^2). Its age, according to the data of a number of investigators, is pre-Upper Jurassic. The Shakhtama granodiorite intrusion is accompanied by various stock-like bodies and numerous granite porphyry, granodiorite porphyry, lamprophyre, syenite and other dikes, and some investigators ascribe the mineralization at the Shakhtama molybdenum deposit to this granodiorite.

The Malyi Soktui massif lies within the boundaries of the tin-tungsten metallogenetic zone (Kubul'bei complex). It is composed of coarse- and medium-grained biotite granite outcropping over an area of 400 km^2. Its reactive contact with the Lower and Middle Jurassic sandstone-shale sequence is exposed.

It can be seen from this account that the amount of feldspar (potash and soda-lime) is more or less the same in all three types of rocks (50-60%). The biotite granite of Malyi Soktui has the highest quartz content (40%). The Klichka quartz diorite and the Shakhtama granodiorite contain considerable amounts of biotite and hornblende. The relatively high content of sphene and magnetite characterizes the Shakhtama granodiorite. These minerals are absent from the Klichka quartz diorite and the Malyi Sokhtui granite. Occasional grains of galena have been found only in the Shakhtama granodiorite.

Lead in the samples was determined chemically. To decompose the sample and to take the lead and some of the minerals into solution, the rock was treated with a mixture of hydrofluoric and hydrochloric or sulfuric acid (monazite).

Zircon was dissolved after fusion with acid potassium fluoride. The fusion was leached with 50% sulfuric acid.

The lead in the analysis of zircon and monazite was concentrated by precipitation of lead and barium sulfates. The sulfate precipitate was converted to carbonates by fusion with soda. The fusion was leached with water and the carbonates filtered off, washed and dissolved in dilute nitric acid.

Magnetite was dissolved by heating the sample in hydrochloric acid.

After the decomposition of the sample, lead was extracted from the solutions obtained by one of these methods--with chloroform at pH 9-10 and in the presence of ammonium citrate in the form of lead dithizonate. It was separated from the organic solvent with 0.02$\underline{N}$ nitric acid. To evaluate the completeness of extraction from a given sample, the radioactive isotope of lead (RaD) was used. The extracted lead was determined polarographically or, in some cases, colorimetrically (with dithizone).

All lead determinations were made in quartz or platinum dishes with specially purified reagents.

The results of lead determination in the rocks and their minerals are

Distribution of Lead in the Minerals of the Investigated Granitoids

Mineral	Percentage of mineral in the rock	Lead content in the mineral, γ	Amount of lead per one gram of rock, γ	Percentage of total Pb in the rock carried by a given mineral	Total Pb in rock
			Quartz diorite, Klichka		
Feldspar	65	15	9.7	69.3	
Quartz	20	4	0.80	5.6	
Biotite	7	12	0.84	5.0	
Hornblende	7	8	0.56	4.0	
Zircon	0.1	250	0.25	1.8	
Total		–	12.15	86.7	14
			Granodiorite, Shakhtama		
Feldspars	62	15	9.3	46.5	
Quartz	25	3	0.75	3.7	
Biotite	6	10	0.60	3.0	
Hornblende	7	14	0.98	4.9	
Zircon	0.07	10	0.01	0.05	
Sphene	0.33	71	0.23	1.1	
Magnetite	1.0	28	0.28	1.4	
Total		–	12.15	60.65	20
			Biotite granite, Malyi Soktui		
Feldspars	54	19	10.45	37.3	
Quartz	40	3	1.20	4.3	
Biotite	5	36	1.80	6.4	
Monazite	0.07	20	0.01	0.05	
Fluorite	0.2	0.9	0.02	0.06	
Total		–	13.48	49.1	28

given in the Table.

It will be seen that the feldspars separated from the granitoids of the different metallogenic zones have very similar lead content. Thus the plagioclases of the Klichka quartz diorites contain 15 γ of lead, the feldspars of the Shakhtama and Malyi Soktui granitoids contain 15 γ and 19 γ Pb, respectively. It should be noted that these figures are somewhat lower than the figures obtained for the lead content in feldspars by L. V. Tauson and L. A. Kravchenko [1] in their investigation of Caledonian granitoids of the Susamyr batholith.

Quartz contains a small amount of lead (3 – 4 γ). The concentration of lead in the biotites of acid intrusives of the different metallogenetic zones ranges from 10 γ to 36 γ. It is noteworthy that the biotite from the tin-bearing Malyi Soktui contains twice as much lead as the feldspars from the same intrusive.

The biotites separated from the granitoids of the polymetallic and molybdenum metallogenetic zones contain a little less lead (10-12 γ). Noteworthy is the relatively high lead content in the zircons of the Shakhtama granodiorites.

These data show that from 37% to 70% of the lead in the investigated rocks is concentrated in feldspars. The fraction of lead in the feldspars decreases from the granitoids of the polymetallic zones to the granitoids of the molybdenum and tin zones. Thus, the plagioclases of the Klichka quartz diorite contain 69.3% of the total lead in the rock, but in the Shakhtama granodiorites this percentage decreases to 46.5%. The lowest concentration of lead was found in the feldspars separated from the granitoids of the Malyi Soktui massif (37.3%).

The same tendency is observed with the lead in the zircons from the three metallogenetic zones*.

It must be noted that the total amount of lead separated from the minerals is lower than its content in the rock samples. This difference increases rapidly from the Klichka quartz diorite to the Malyi Soktui granite in spite of the higher potash feldspar content in the latter.

The majority of the accessory minerals (sphene, zircon, magnetite, fluorite, apatite) play a negligible role in the distribution of lead in the rocks. Galena occupies a special place for the presence of even occasional grains of this mineral affects the total amount of lead.

In their study of the distribution of lead among the minerals of the granitoids of the Susamyr batholith, Tauson and Kravchenko [1] showed that lead is concentrated in the granitoids, mainly in the feldspars, and stated that only in the potash feldspars does it occur almost entirely as a diadochic substitute. A considerable amount of lead in the rock occurs in an easily leachable "extra-silicate" form, possibly in submicroscopic grains of galena or native lead.

In the rocks described here, galena was found in the Shakhtama granodiorite. Its content in this rock is about 0.001%.

It may be supposed that the higher lead content in the tin-tungsten zones (sample from Malyi Soktui) as compared with similar rocks in other metallogenetic zones is due to the presence of minute crystals of galena (< 0.05 cm).

It was mentioned earlier that the amount of lead in feldspars diminishes from the granitoids of the polymetallic zones to the granitoids of the tin-tungsten zones. The opposite appears to be true of lead in the form of galena.

The amount of lead carried in galena increases from the granitoids of the polymetallic zones, quartz diorites (~14%), to the granitoids of the tin-tungsten zones, biotite granites (~52%).

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*It is interesting to note that the zircons of the Klichka quartz diorite have a relatively high lead content concentrated in minute inclusions of galena. The isotopic composition of the lead separated from this zircon corresponds to that of hydrothermal lead. Perhaps these zircons are of hydrothermal origin. This hypothesis, however, requires further investigation.

Evidently the importance of primary ("magmatic") lead in the general balance of lead in the rock is considerably greater in the granitoids of the polymetallic zones (~85%) than in the granitoids of the molybdenum (~60%) and tin-tungsten zones (~48%).

On the other hand, it should be noted that the Klichka quartz diorite (polymetallic zone) has a lower lead content than the tin-bearing Malyi Sokotui granite. Evidently the rocks which, according to the geological data, are responsible for the polymetallic mineralization are not always marked by high lead content.

Thus, the study of the character of distribution of lead in the minerals of some granitoids of the three metallogenetic zones of Eastern Transbaikalia --polymetallic, molybdenum and tin-tungsten-- shows that: 1) from 37 to 70% of the total lead is concentrated in the feldspars of the granitoids; 2) there is a certain tendency for the lead content in the feldspars to diminish in passing from the granitoids of the polymetallic zone to those of the tin-tungsten zone but that the reverse is true for the lead occurring as galena; and 3) the quartz diorite of the polymetallic zone has a lower lead content than the granite of the tin-tungsten deposit.

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AN EXPERIMENT IN BIOGEOCHEMICAL SAMPLING AND THE METHOD OF DETERMINATION OF NIOBIUM IN PLANTS

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(ABSTRACT)

An increase of the niobium content in plants from 0—3 μg to 50—70 μg (per 5 g of dry plant material) may serve as an indication for search in geological-prospecting work.

It is found that in the region under examination Rubus arcticus L., Chamaenerium angustifolium L., Vaccinium myrtillulus L., and Rubus chamaemorus L. show the greatest ability for niobium extraction from the soil.

Methods of the determination of niobium, both from ash and from dried plant material are worked out.

The biogeochemical method of prospecting for ores is widely used in the Soviet Union, thanks to the work of A. P. Vinogradov [1-3], D. P. Malyuga [4], S. M. Tkalich [5] and others.

There is no mention in the literature of the use of the biogeochemical method in the search for niobium deposits. We carried out our investigation in the region of Srednii Timan, Komi ASSR, where a rare metal mineralization was accompanied by high concentration of niobium. The region had been studied in detail by both the metallometric and geophysical methods.

We checked the possibility of using the biogeochemical method under the local conditions. Inasmuch as the niobium content in the plant matter is low, we concentrated the microgram quantities of niobium with $MnO(OH)_2$ as the

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*A. Ya. Fedotova (Western Geophysical Organization) took part in the experimental work.

collector. The technique of concentrating trace elements is widely used now [6]. The manganese dioxide is often used as an active nonspecific adsorbent for many products of nuclear reactions including Nb^{95} [7].

The data obtained by us from standard solutions are represented by the graph of Fig. 1, which shows that with the content of 5 to 50 μg Nb_2O_5 in 400 ml of solution, the efficiency of precipitation with manganese dioxide reaches 100%. When the content of niobium increases, the efficiency of precipitation decreases to 75%. The determinations of niobium were made by colorimetry of the thiocyanate complex [8, 9]. The color of the thiocyanate complex is affected by Mo, W, Pt, Hg, U, V, Ti and P.

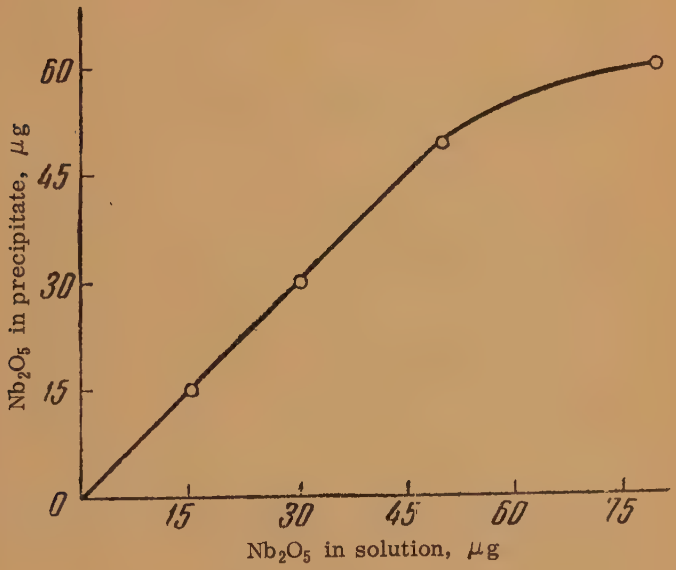

Fig. 1. Precipitation of niobium with manganese dioxide

The unconsolidated deposits of the region do not contain Mo, W, Pt and Hg. According to Ward and Marranzino [9], U, V and Ti in amounts not exceeding 1000, 100 and 400 μg, respectively, do not interfere with the determination of niobium when its content is between 0 and 20 μg.

Our tests showed that such quantities of V and Ti were not present in the 7 g samples of dry plant matter. According to Vinogradov, the content of uranium in plants growing over the deposit is $1 \cdot 10^{2}\%$, and therefore the effect of uranium was neglected in our investigations. The main difficulty in the determination of Nb was the high content of the PO_4^{3} ion, but we found that when niobium is precipitated with $MnO(OH)_2$ in an acid medium the content of PO_4^{3} is reduced from 40 to 50 times. One of the most strongly interfering elements in niobium determination is molybdenum. Even a fivefold excess of Mo over Nb presents a serious difficulty [9].

Molybdenum was absent from the plants investigated by us, but it was noticed that if a concentrate obtained in an acid medium and containing both Nb and specially added Mo is dissolved and reprecipitated* in a medium containing 4% $NaCO_3$, the Mo content in the concentrate is diminished. Determination of Nb in this case is possible when Nb:MO = 1:30. The reprecipitation decreases the amount of niobium available for determination by about 20%. It must be borne in mind that if $MnO(OH)_2$ with the adsorbed Mo and Nb is allowed to stand in an alkaline medium for over one hour, both Mo and Nb go into solution.

THE SPECTROPHOTOMETRIC METHOD OF DETERMINATION OF NIOBIUM

Ash analysis

A 5 to 7g sample of dry leaves was used for analysis.** The leaves were reduced to ash and the ash was fused with 8 to 10 times as much $KHSO_4$. The fusion was leached with 40 ml of saturated $(NH_4)_2C_2O_4$, transferred together with the residue to a 500-600 ml beaker, and 300 ml of water and 20 ml conc. HCl was added to it. Then the solution was brought to a boil, and 1N solution of $KMnO_4$ (~ 20 ml) was slowly poured into it until the formation of flaky $MnO(OH)_2$. The amount of manganese dioxide formed was of the order of 200-300 ml. After the precipitate settled the solution was siphoned off. The residue containing adsorbed niobium was dissolved in a mixture of 6% H_2O_2 with a few drops of conc. HCl. The solution was transferred to a quartz dish and evaporated to dryness on a water bath. The determination of niobium was made by the thiocyanate method [8, 9]. The colorimetric measurements were made on a quartz spectrophotometer SF-4 in silica cells with a 10 mm light path and λ = 380 mμ. Calibration curves were constructed beforehand.

Analysis without reduction to ash (oxalate extract)

If the niobium content in the plants was relatively high, 2 to 3g of dried leaves were used for analysis; if low, 5 to 7g. The leaves were ground up carefully and covered with 100 ml of 2% $(NH_4)_2C_2O_4$. By adding HCl, the ph of the extract was brought to 4.5 - 5. The mixture was boiled for 20 min., brought to 200 ml with hot water and allowed to stand for 10 - 12 hours. The extract was filtered off from the plant matter which was previously washed with 100 ml of hot water. The heated solution was acidified with 15 ml conc. HCl, and 1N $KMnO_4$ solution was added until formation of flaky $MnO(OH)_2$. After dissolving the manganese dioxide in a mixture of H_2O_2 and HCl, the solution was evaporated to 1 - 1.5 ml. If the residue was dark, it was treated with several drops of 20 - 30% H_2O_2 and evaporated again to 1 - 1.5 ml. The remaining H_2O_2 was decomposed with a few drops of 10% solution of $SnCl_2$ in 2N HCl, and a hydrochloric-tartaric acid solution was added. Since very often the organic compounds are not completely decomposed, it is necessary before adding ammonium thiocyanate to shake the solution once or twice with ether until a colorless ether layer is obtained. The determination was completed by the thiocyanate method [8, 9].

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*More precisely, precipitated with manganese dioxide, which forms in the presence of H_2O_2.

** When the niobium content is relatively high (5-6 μg of Nb_2O_5 per gram of plant matter) 2 to 3g of dried leaves suffice. In this case Nb is determined by the usual thiocyanate method [8, 9].

SPECTROGRAPHIC DETERMINATION OF NIOBIUM

The hydrochloric acid solution of the concentrate obtained in the course of analysis of ash of 40g of dry leaves was analyzed spectrographically.

The spectra were photographed on the ISP-28 spectrograph with an AC arc operated at 220 volts and 5 amps. as the light source. Spectrographically pure carbon electrodes and iso-orthochromatic plates with a sensitivity of 65 GOST units were used. The exposure was 30 seconds. The determination of concentration was made by comparison with standard spectra prepared for 20, 40, 60, etc. μg concentrations of Nb_2O_5. The analysis was based on the 3130, 3094, 2951 and 2927 A Nb lines. The samples were prepared for spectrographic analysis by the well-known method described in reference [10].

A comparison of the results of spectrophotometric and spectrographic analyses is given in Table 1.

Table 1

Sample number	By spectrophotometry	By spectrography	
	Nb_2O_5 in 7 g of plant matter, μg	Nb_2O_5 in 40 g of plant matter, μg	Nb_2O_5 in μg calculated for 7 g of plant matter
I	20	80	14
II	12	60	10
III	10	40	7

All data are based on two analyses of the same concentrate. The difference between two determinations by the spectrographic method was ± 20%, and by the spectrophotometric method, ± 5 — 10%.

To check the method determinations of Nb added to plant matter were made (Table 2).

Tables 1 and 2 show that either spectrography or spectrophotometry may be used as the final step in analysis (in either case the relative error did not exceed ± 30%).

Table 2

Sample number	By spectrophotometry			Sample number	By spectrography		
	Nb_2O_5 in sample, μg	Nb_2O_5 added, μg	Nb_2O_5 found, μg		Nb_2O_5 in sample, μg	Nb_2O_5 added, μg	Nb_2O_5 found, μg
1	none	5	4.5	1	none	100	100
2	none	10	12	2	none	100	100
3	none	50	46	3	none	50	60
4	25	5	31	4	25	50	100
5	26	10	35	5	26	50	100

RESULTS OF BIOGEOCHEMICAL SAMPLING

We analyzed plants growing throughout the region under investigation.

In order to find plants possessing the greatest capacity for accumulating niobium, 10-40 samples of each species* were analyzed.

The percentage of plants having a given niobium content in relation to the total number of analyzed samples of a given species is given in Table 3.

Table 3 shows that high niobium content was found in the following plants: Rubus arcticus L., Vaccinium myrtillus L., Chamaenerium angustifolium L., Betula pubescens and Betula verrucosa. A low niobium content was found in Sphagnum, Salix, Picea obovata L., Carex vesicaria and Ribes nigrum.

The results of analyses of 200 samples of different plant species indicate that, with the exception of Rubus arcticus, more than 50% of each species has Nb_2O_5 content ranging from 0 to 3 μg per 5g of dry leaves. This content was taken as normal. The Nb_2O_5 content in plants growing in the mineralized zone is shown in columns 3 - 6 of Table 3. For some species the adsorption of niobium by different parts of the plant was investigated.

As a rule the content of niobium in leaves is higher than in branches and twigs. The niobium content in the roots was checked only for Chamaenerium angustofolium and was found to be about 2 or 3 times as high as in the leaves. It should be noted that the highest niobium content in leaves was observed in the segments of the profile lying over the faults responsible for the mineralization (Fig. 2).

Summary

1. A method has been developed for determination of niobium both in the plant ash and in the dried plant matter.

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* Plants analyzed on fewer than 10 samples are not listed in Table 3.

Table 3

Plant	Percentage of plants with equal Nb_2O_5 content in 5 g of dry leaves						Total number of samples
	Nb_2O_5 content in μg						
	0 to 3	4 to 5	6 to 7	8 to 17	8 to 25	8 to 60	
Betula pubescens Ehr. and B. verrucosa Ehr.	56	33	1.5	9.5	-	-	40
Sphagnum Sp.	70	30	-	-	-	-	20
Vaccinium myrtillus L.	70	13	-	17	-	-	15
Chamaenerium angustifolium L.	57	7	8	-	28	-	20
Picea obovata L.	79	21	-	-	-	-	15
Rubus arcticus L.	21	15	14	-	-	50	20
Carex vesicaria L.	85	15	-	-	-	-	15
Ribes nigrum L.	85	15	-	-	-	-	10
Salix Sp.	63	22	15	-	-	-	20

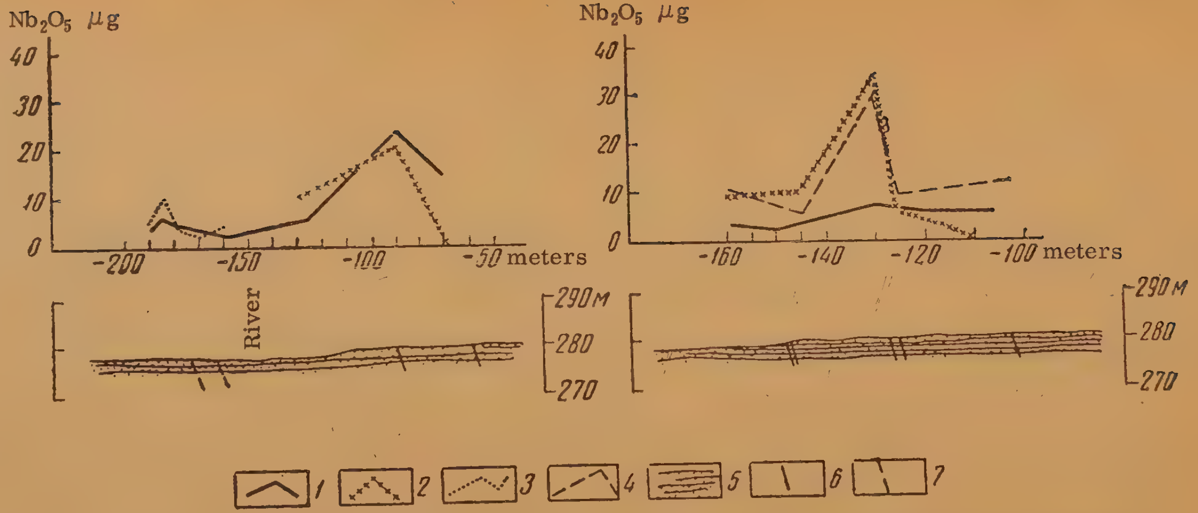

Fig. 2. Results of determination of Nb_2O_5 in 7g samples of dry plant matter from the mineralized area

1 -- Betula pubescens Ehr., 2 -- Chamaenerium angustifolium L., 3 -- Lonicera coerulea L., 4 -- Rubus arcticus L., 5 -- bedrock: quartzites and schists, 6 -- orebodies disclosed by mining, 7 -- location of new orebodies according to geophysical and geological data

2. Relatively high niobium content was found in plants, ranging from 0 – 3 μg to 50 – 70 μg (per 5g of dry plant matter); and this may serve as a guide to ore in exploratory geological work.

3. It was found that the greatest capacity for extracting niobium from the soil in the investigated region is possessed by: Rubus arcticus, L., Chamaenerium angustofolium L., Vaccinium myrtillus L. and Rubus Chamaemorus L.

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BRIEF COMMUNICATIONS

THE AGE OF THE OLDEST ROCKS OF ANTARCTICA

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The geological data available at present indicate the probability of the existence in the Soviet sector of Antarctica of the oldest Precambrian rocks.

This is indicated by the numerous outcrops of metamorphic rocks, intensively dislocated gneisses and ferruginous quartzites, and by the first determinations of the absolute age of biotite from the gneisses made in 1958 by Goldich, Nier and Washburn, which gave an argon age of 520 million years for the gneisses in the region of McMurdo Sound.

We investigated specimens of allanite, biotite and muscovite from the pegmatites in the region of Mirnyi, which cut a sequence of gneisses and ferruginous quartzites. The specimens were kindly presented to us by a member of the Antarctic expedition, E. I. Chervov.

The allanite was a single crystal 3 x 1.5 x 0.6 cm^3. Its central part, free from the brown alteration products which formed a film on the surface of the crystal, was sawn out. The microscope showed a little included magnetite and thin carbonate veinlets in the allanite. The mineral was almost completely isotropic. The biotite and muscovite were 5 x 3 cm^2 plates and esceptionally fresh.

The age determinations of allanite by the lead-uranium-thorium method and of biotite and muscovite by the potassium-argon method gave very similar results (see Tables 1 and 2), indicating magmatic activity in this part of Antarctica about 1300 million years ago. The most probable age of the minerals is 1300 ± 100 million years.

Because of the low uranium content in allanite and the correspondingly low Pb^{207} content, which would be particularly affected by inaccuracy in the correction for common lead, it is believed that the Pb^{206}/U^{238} and Pb^{208}/Th^{232} ratios gave more reliable ages.

Inasmuch as in the marginal parts of the Precambrian shields of the nearby Australia and Africa, igneous rocks and ores had previously given similar ages (Isa Mine, Australia, 1190 million years; Kagadi, Africa,

Table 1

Age of Allanite

	Pb	U radiochemical determination	Th radiochemical determination	
Content of components, wt. %	0.1	0.011	1.5	
	Pb^{204}	Pb^{206}	Pb^{207}	Pb^{208}
Isotopic composition of lead in the mineral	0.077	3.35	1.27	100
Correction for common lead	(1.0) 0.077	(16.59) 1.28	(15.49) 1.19	(36.13) 2.53
Isotopic composition of radiogenic lead in the mineral	–	2.07	0.08	97.47
Content of isotopes of radiogenic lead in the mineral, %	–	0.002	0.00008?	0.0931
	$\frac{Pb^{207}}{Pb^{206}}$	$\frac{Pb^{206}}{U^{238}}$	$\frac{Pb^{207}}{U^{235}}$	$\frac{Pb^{208}}{Th^{232}}$
Isotope ratios	0.04	0.2	1.14	0.07
Age, 10^6 years	?	1190	(800)	1350

Note. Correction is based on the isotopic composition of common lead corresponding to the theoretically calculated composition of lead in the earth's crust 1200 million years ago.

1370 million years), it is reasonable to suppose that the ages obtained for Antarctica confirm an intensive magmatic activity in this part of the southern hemisphere about 1300 million years ago.

Table 2

Age of Micas

Mineral	Content of components		Age in million years
	Potassium, wt. %	Argon, 10^{-4} cm^3/g	
Biotite	7.04	5.10	1330
Muscovite	7.70	5.27	1280

Note. In computing ages the following constants were used: $\lambda_K = 5.50 \cdot 10^{-11}$ years^{-1}; $\lambda_\beta = 4.72 \cdot 10^{-10}$ years^{-1}; $K_{40}/K_{41} + K_{39} = 1.22 \cdot 10^{-4}$

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BRIEF COMMUNICATIONS

ON THE NATURE OF CARBURAN

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(ABSTRACT)

Carburan is found to be a radioactive vein bitumen, being a mixture of uraninite (pitchblende) and hydrocarbon, and to form metasomatically in the hydrothermal stage of a pegmatite process.

The most probable source of carburan carbon is the including graphite gneisses, i.e., the carbon is of organic origin and hydrothermal by its genesis.

For the above mentioned group of substances having been formed in this way the name "carburan" is proposed.

An investigation of a series of carburan-bearing pegmatite dikes and of the composition and structure of carburan suggests certain ideas concerning its origin. A mineragraphic examination by reflected light shows that the gray carbonaceous mass of carburan is traversed by a network of very fine cracks, often filled with pyrite and chalcopyrite. The strongly anisotropic carbonaceous mass has wavy extinction and contains numerous randomly distributed anhedral isotropic grains of uraninite, locally forming rather considerable areas (Figs. 1 and 2). The size of the grains is from 0.001 to 0.03 mm. Some of the larger grains have fractures, often filled with sulfides. Frequently uraninite contains anhedral grains of galena and even of native lead. In some polished sections there are rather regular square areas containing narrow light and dark bands. The uraninite grains form chains within the dark bands (Fig. 2). Rotation of the stage between crossed nicols causes extinction of alternate bands (Fig. 3) resembling the effect produced by polysynthetically twinned plagioclase. Sometimes the bands containing uraninite exhibit between crossed nicols a peculiar grid structure of the "microcline" type. The ash content of carburan is very variable but is always between 4.19 and 28.13%. These are the extreme values for all known carburans [1-5]. According to spectrographic analyses, all specimens of carburan contain Co, Ni, Cu, Zn, Bi, Ag, Pb, Ba, and Sr,

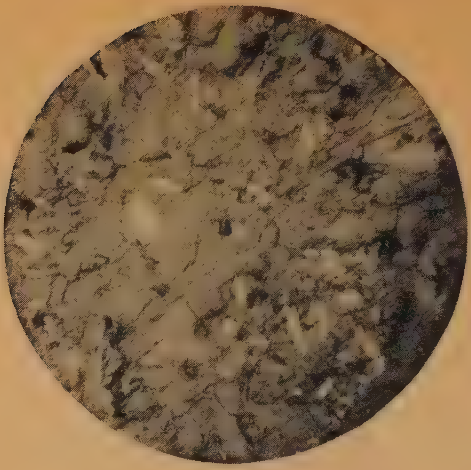

Fig. 1

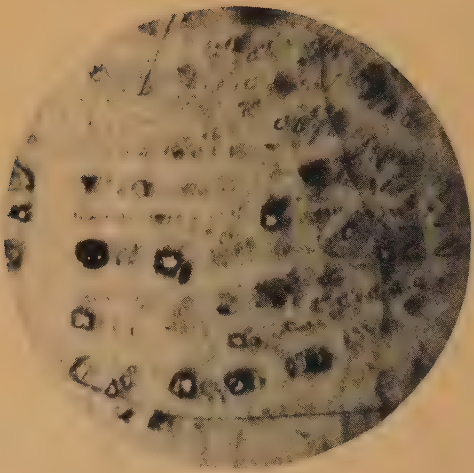

Fig. 2

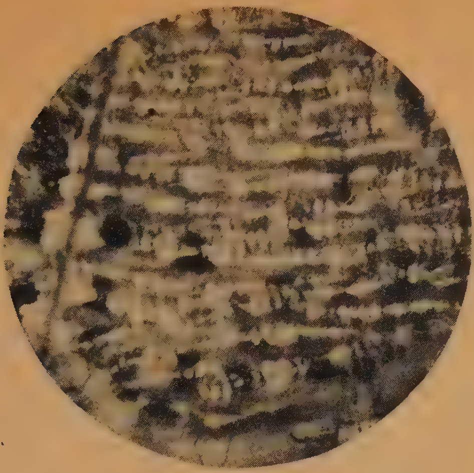

Fig. 3

which are irregularly distributed and occur in small amounts. In the sulfides associated with carburan, Co and Ni occur in pyrrhotite and in pyrite, and Co, Ni, Ag, Zn, Pb, and Bi, in chalcopyrite. Hence the occurrence of these elements in carburan is explained by the presence of sulfide inclusions.

An x-ray analysis for rare earths in carburan was made by N. V. Turanskaya (Institute of Geochemistry and Analytical Chemistry). Taking the Nd content as unity, the content of the other rare earths is as follows: 1: Nd--1, Sm--1, Gd--1, Dy--1.1, Y--4.7 and Er--0.47. The content of the remaining lanthanides is below the sensitivity of the spectrograph. These data are similar to those obtained by other authors [5-7].

In explaining the origin of carburan, most investigators advance a "radiochemical polymerization" hypothesis based on the assumption that the radioactive element causes polymerization of gaseous and liquid hydrocarbons into solid products [2, 3, 4, 8].

In the author's opinion this hypothesis quite erroneously ascribes the decisive role in the formation of carburan to the polymerizing effect of radioactive elements. More likely, polymerization and solidification are not caused by radioactivity, for solid colloform hydrocarbons free from radioactive elements are common [9-12], but by the natural process of aging of the hydrocarbon colloids, which perhaps is aided by radioactivity.

The following outline of formation of carburan is proposed here:

1. Carburan was deposited during the hydrothermal stage of the pegmatitic process (pyrrhotite-carburan mineralization) from mobile hydrocarbon solutions.

2. The hydrocarbon mass was polymerized and solidified with simultaneous separation of uraninite (pitchblende). The formation of cracks and their filling with pyrite and chalcopyrite took place in the final stages of the pyrrhotite-carburan mineralization. The galena found in intimate association with chalcopyrite and containing nonradiogenic lead shows that this mineralization was contemporaneous with the formation of the pegmatite

(1850 million years ago) [13].

3. A superimposition of a later hydrothermal process caused recrystallization of carburan with separation of radiogenic lead, whose isotopic composition dates this process as having occurred 500-700 million years ago [13].

This outline makes understandable the formation of thucholite pseudomorphs after tourmaline, described by Ellsworth, which cannot be explained by the "radiochemical polymerization" hypothesis.

The most probable source of carbon in carburan is the enclosing graphite gneisses; i.e., the carbon of carburan is organic in origin but hydrothermally redeposited. This is confirmed by the disappearance of graphite from the gneiss near the pegmatite dikes containing carburan.

To avoid terminological confusion ("uranium-bearing hydrocarbon," "uraninite hydrocarbon complex," "carbon," "carbocer," "thucholite," "carburan"), this group of "minerals" should be designated by the single term "carburan," introduced into the literature by A. N. Labuntsov as far back as 1927. It should be borne in mind that the composition of carburan is identical with that of the majority of radioactive hydrocarbons, and the name is logical since it suggests the two essential components of these "minerals"--carbon and uranium.

The author takes this opportunity to thank his adviser, K. K. Zhirov, and also S. S. Borishanskaya, N. T. Voskresenskaya and L. A. Borisenok, for their assistance in this research.

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REVIEW

V. M. KREITER, V. V. ARISTOV, I. S. VOLYNSKII,
A. B. KRESTOVNIKOV and V. V. KUVICHINSKII
"POVEDENIE ZOLOTA V ZONE OKISLENIYA ZOLOTO-SUL'FIDNYKH MESTOROZHDENII
Gosgeoltekhizdat, Moscow, 1959, 268 pages
Price, 13 r. 90 k.

There are many gaps in our knowledge of the geochemistry of gold which eed filling. The problem of the circulation of gold in the earth's crust has ot been solved: great amounts of gold dissolved by ground waters are car- ied out into seas and oceans, but its further history is not known. In gen- ral, the sedimentary rocks contain very little gold, and this means that it s preferentially precipitated somewhere from marine waters. Perhaps e deposits of the Rand in South Africa, colossal in reserves and richness, ere formed from marine sediments.

There are many other unsolved problems in the geochemistry of gold. re there two gold fractions deposited in hydrothermal veins, an early and late one, or is there only one? Can gold be carried by hot solutions over rge distances? What role is played by colloidal suspensions in the trans- r of gold? And so on. The solution of some of these problems would ve not only purely scientific but also practical value.

One of these still incompletely solved problems in the geochemistry of ld is the problem of the solution of gold in the oxidized zones of sulfide posits and of precipitation of secondary gold in the underlying zone of mentation. The authors of the book reviewed here made a thorough study these processes.

In the words of the authors--geologists, mineralogists and chemists ited under the guidance of V. M. Kreiter--the object of their work was to ive the investigators a practical basis, following from the ideas concern- g the supergene migration of gold, for determining the primary and sec- dary zones of gold deposits."

The first chapter of the book gives a summary of the modern concepts of pogene and supergene gold and makes it evident that there are many dif- rent opinions about the origin of hydrothermal gold and its later history in e zone of weathering.

The second chapter presents the results of geological and mineralogical servations at the Maikain (Kazakhstan), Dzhugaly (Kazakhstan), Blyava d Novyi Sibai (Southern Urals) deposits. The observations include geol- y, mineralogy and geochemistry of gold in the oxidized zone. There are merous sketches of polished sections of minerals, including secondary gold. From the material of this chapter, an entirely correct conclusion is drawn that secondary (supergene) gold can form in considerable quantities only if sulfides are present in the primary ores containing microscopic and submicroscopic gold.

The third chapter describes the formation of secondary auriferous zones. A general account is given of the formation of different minerals in the zone where the solutions descending from the oxidized zone enter a reducing environment. Here supergene gold is deposited in a variety of forms and compositions, together with argentite and, less commonly, native silver.

The process which interested the authors the most is that of the solution of gold in the oxidized zone. Experiments and calculations were made to discover the possible solvents of gold and the rates of solution.

The results of these experiments and calculations are given in chapter four. They show that gold may be dissolved in "geologically short time" in acid solutions of ferric sulfate, in iron chloride solution and in hydrochloric and nitric acids, provided it is finely dispersed. Under the same conditions, gold dissolves much more slowly in sulfuric acid.

Very interesting is the method used by the authors in the study of the solubility of gold. They prepared thin films of metallic gold on glass, which were dried and heated to the melting point of glass.

It is shown by calculations what volume of water or of some other solvent is required to dissolve a given weight of dispersed gold. For water, the volume is very large, but for iron chloride or ferric sulfate solutions, it is relatively small. From this, the time required to dissolve 10g of coarse gold dispersed through a block of ore (0.4 m^3) is calculated and found to be from 2000 to 35000 years, depending on the concentration of the solution.

Chapter five contains a description of the conditions of solution and migration of gold in the oxidized zone. Here the authors review the literature on the subject and give their conclusions. They consider that solution of dispersed gold in $Fe_2(SO_4)_3$ and sulfuric acid is the most probably mode of transfer of gold. The solution of gold in iron chloride is regarded as less probable by the authors. The behavior of silver, which migrates with gold or a little ahead of it, speaks in favor of the first hypothesis. The authors discard as improbable and contradictory to observation and experiment the hypothesis of F. Freize of the transfer of gold in organic solvents, that of A. E. Fersman of its migration in the form of cyanides, F. V. Chukhrov's idea that gold is transported in the form of bromides and iodides and M. N. Al'bov's hypothesis of the transfer of gold in suspensions.

The authors document their opinion by observations made at the deposits.

The last two chapters are essentially appendices to the main text. In the sixth chapter there are notes on the practical methods of valuation of gold ore outcrops and in the seventh, some methodological questions of mineragraphy of gold ores are discussed.

Chapter five, which summarizes the findings of the authors, is of especial interest to geochemists. Can the authors' main conclusion that gold is dissolved in the sulfates in the oxidized zone be regarded as proved? Not quite, the reviewer believes. Undoubtedly the migration of gold from the oxidized zone into the underlying rocks is connected with the presence of sulfates and dispersed gold in it. There is no doubt that as a result of oxidation of sulfides free sulfuric acid and ferric sulfate are formed. The authors' experiments have proved that ferric sulfate in a sulfuric acid environment will dissolve gold.

But under natural conditions gold may be dissolved in hydrochloric acid formed from the action of sulfuric acid on sodium chloride. This process is definitely stimulated by the oxidizing action of $Fe_2(SO_4)_3$. The authors of the book consider solution in hydrochloric acid and ferric sulfate improbable and refer to the behavior of silver migrating together with gold. Gold chloride, in the authors' opinion, would remain in the oxidized zone. But they forget that silver chloride is itself easily dissolved by solutions of sodium chloride in hydrochloric acid, forms complex compounds and may migrate into the zone of cementation together with gold. The argument based on the behavior of silver is therefore not decisive.

The reviewer would accept the authors' view of the migration of gold in the form of sulfate solutions as true if they had proved the existence of compounds of gold with ferric sulfate and sulfuric acid and had studied its properties. They have not done this but merely remarked that the formation of complex compounds is probable. Their hypothesis remains a hypothesis. Speaking of the solution of gold in ferric sulfate-sulfuric acid solutions, the authors remark (p. 215) that the presence of chlorides hastens solution. This argues a greater probability of solution of gold in hydrochloric acid formed under the oxidizing action of $Fe_2(SO_4)_3$. Complex chloride compounds of gold which may form under these conditions, such as $Na[AuCl_4]$, are known, and others are possible, including those mentioned in the book on p. 207.

These comments indicate that some points have not been sufficiently developed in the book but are not intended to belittle its importance. The book is very interesting, gives abundant factual material, discusses a difficult problem from many points of view and contains practical and methodological suggestions usable in field and laboratory work.

The publication of the book should be welcomed and the authors encouraged to continue their investigations.

The book is quite satisfactorily designed, but the editors passed a number of misprints, some of them rather annoying (for example, the formulas on pp. 207 and 298, the symbol m^3 on p. 217, the initials of K. F. Beloglazov on pp. 227 and 263, etc.). The photomicrographs (pp. 250-251) are not at all clear and should have been printed on an insert.

May 20, 1959 O. Zvyagintsev

NEWS

VIII SESSION OF THE COMMITTEE FOR DETERMINATION OF THE ABSOLUTE AGE OF GEOLOGICAL FORMATIONS (DIVISION OF GEOLOGICAL AND GEOGRAPHICAL SCIENCES), ACADEMY OF SCIENCES USSR, May 18-22, 1959, Moscow

The Eighth Session of the Committee for Determination of the Absolute Age of Geological Formations took place at the V. I. Vernadskii Institute of Geochemistry and Analytical Chemistry, in Moscow, on May 18-22, 1959.

The extensive work on the determination of the absolute age of the principal rock complexes in several regions of the USSR, successfully carried out by the central laboratories and those of the constituent republics, made it possible to generalize age data and to select a series of reports by various collectives to be presented at the XXI International Geological Congress. These reports aroused much interest and discussion at the meetings of the Committee.

The list of these reports given below indicates the scope of age determinations in the most important regions of the USSR.

A. V. Polkanov and E. K. Gerling: "Problems of the Absolute Age of the Precambrian of the Baltic Shield." On the basis of about 500 determinations, mainly by the A-K method, the authors have separated 13 age groups in the interval between 3500 and 300 million years.

The Committee found it necessary to select two reports on the geochronology of the Ukrainian crystalline shield for presentation at the International Congress: A. P. Vinogradov, L. V. Komlev and A. I. Tugarinov: "Absolute Age of the Rocks of the Ukrainian Crystalline Shield," and P. P. Semenenko, E. S. Burkser and M. N. Ivantishin: "Age Groups of Mineralization of Ukrainian Rocks according to Absolute Chronology."

A. P. Vinogradov, A. I. Tugarinov, K. G. Knorre and E. V. Bibikova, V. V. Zhirova and S. I. Zykov: "The Age of the Precambrian Rocks of the Crystalline Basement of the Russian Platform." This report gives a correlation of intrusive and metamorphic complexes of different parts of the basement of the platform, with previously dated similar intrusives of the Baltic and Ukrainian shields.

I. E. Starik, A. Ya. Krylov, M. G. Ravich and Yu. I. Silin: "The Absolute Age of the Rocks of Eastern Antarctica." The territory is divided into eight age groups, ranging from 50 to 1450 million years.

A. Ya. Krylov: "The Absolute Age of the Rocks of Central Tien Shan and the Application of the Argon Method to Metamorphic and Sedimentary Rocks." A report of great geological and methodological interest.

G. D. Afanas'ev: "A Geochronological Summary of the Rocks of the Caucasus." This paper discusses the sequence of magmatic events in this complex territory and establishes the presence of four groups of intrusives of different ages.

L. P. Ovchinnikov and M. A. Garris: "The Age of Geological Formations of the Urals and Pre-Urals." This is a combined report of the laboratories of the Uralian and Bashkirian affiliates of the Academy of Science.

N. I. Polev, G. A. Nurina and G. A. Kazakov: "The Determination of the Absolute Age of Sedimentary and Volcanic Formations."

L. P. Krasnyi and N. I. Polevaya: "The Absolute Age of the Igneous Rocks of the Far East." This is a summary of the investigations carried out over many years on the geochronology of the Far East.

L. V. Komlev: "The Absolute Age of the Granitic Intrusives of Kazakhstan."

As in the preceding session, considerable attention was given to the methodological work done in a number of laboratories (RIAN GEOKhI, LAGED, VSEGEI, UFAN and others). Here an interesting paper by E. K. Gerling and Yu. A. Sukolyukov should be noted on the accumulation of A^{38} in uranium inerals, and the report of the Age Determination Laboratory of the Geological Institute, Academy of Sciences, Georgian SSR, on the method of isotope dilution and flame photometry.

Serious consideration was given at the meetings to the problem of dating of sedimentary rocks and great interest was aroused by A. Ya. Kylov's paper, in which he demonstrated good preservation of radiogenic argon in detrital materials (pebbles, sands, sandstones, clays and oozes).

Considerable interest was aroused also by A. I. Tugarinov and S. I. Zykov's report on the first attempt at dating carbonate rocks by the isotopic composition of lead.

D. I. Shcherbakov reminded the meeting of the decision taken at the VI session to systematize age determinations on cards, which would help to refine stratigraphic sections and lead to the building of the Soviet scale of absolute chronology.

I. E. Starik reported on the results of control age determinations in a number of laboratories on standard samples of biotite, muscovite and microcline selected under G. D. Afanas'ev's guidance.

The results obtained by the different laboratories show good agreement. This indicates that the technique and method of radioactive dating may be regarded as fully reliable. It was pointed out in this connection that greater accuracy is needed in relating the dated material to geological and stratigraphic data.

An active part in the meetings was taken by J. L. Kulp, Professor at Columbia University. His paper on the new geochronological scale aroused lively interest. A number of very valuable suggestions illustrated by factual material were made by the listeners.

Among the decisions made at the VIII session, one was especially emphasized--to begin a compilation of a Soviet geochronological scale under the general guidance of the Committee on the Determination of the Absolute Ages of Geological Formations. It was decided to use the well-known Holmes scale with possible corrections and additions by Soviet scientists as the basis for the Soviet scale.

V. I. Baranov
K. G. Knorre

Geokhimiya began publication in 1956 under the able editorship of A. P. Vinogradov. It is the Soviet counterpart of *Geochimica et Cosmochimica Acta*, having practically identical fields of interest and coverage and publishing approximately the same number of pages per year. With the great increase in geochemical research in the U. S. S. R., there have come into being a number of highly specialized journals in geochemistry and related fields. It is probably better to begin translating this more general journal first and follow with some of the more specialized ones if interest appears to justify this course of action and if the financial arrangements can be made.

An initial grant from the National Science Foundation in 1958 enabled the Geochemical Society to translate and publish the eight issues for that calendar year. These issues have been very well received by a growing list of subscribers in most of the countries of the Western world.

The issues for 1956 and 1957 have been translated and may be ordered from the Society, c/o Translation Editor, at current subscription prices (see inside front cover).

The National Science Foundation has continued to be most cooperative in this venture. They are continuing support of the project although subscriptions are too few to make it anything like self supporting thus far. It is hoped that subscribers will call attention of other interested workers to the availability of the translation of *Geokhimiya* so that these important research papers can be made more generally available to those interested in geochemical and related investigations.

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In matters of subscription for *Geokhimiya* refer to: Moskva K-104, Pushkinskaya, 23, Akademkniga. Chief Editor: A. P. Vinogradov. Editorial Council: V. I. Baranov, K. A. Vlasov, V. I. Gerasimovskii, D. S. Korzhinskii, A. A. Saukov, N. I. Khitarov (Responsible Secretary), V. V. Shcherbina (Deputy Chief Editor).

Geochemical News is an informal bi-monthly newsletter published by the Geochemical Society and sent without charge to all of its members. It contains news of the activities of the Society, such as summaries of Council Meetings, reports of committees and plans for the future. It also includes announcements of forthcoming meetings and symposia of interest to geochemists, personalia, announcements or short reviews of books of geochemical interest, information on translations and translation services, letters and short notes by members, etc.

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Individuals who wish to receive the *News* should join the Geochemical Society. Application blanks are available on request from the Secretary, Dr. F. R. Boyd, Geophysical Laboratory, 2801 Upton Street, N. W., Washington 8, D. C. Dues are $2.00 per year.

Geochimica et Cosmochimica Acta is the official journal of the Geochemical Society. It is an international journal interested in the broad aspects of geochemistry, both geographically and subject-wise; articles have been received from contributors from all of the (inhabited) continents.

New chemical data and interpretations involving chemical principles are emphasized. For example, papers in chemical mineralogy, petrology, oceanography and volcanology are acceptable, as are those in the chemistry of meteorites, whereas it would be suggested that those in descriptive mineralogy and volcanology, petrography, physical and biological oceanography and physical meteoritics, be sent to other journals specializing in these subjects.

Thus, the subject coverage is closely similar to that of *Geokhimiya*. Also, the number of pages published per year is of the same order of magnitude. Subscription prices are as follows:

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